

UV ABSORBER COMPOSITIONS COMPRISING A HYDROXYPHENYLTRIAZINE COMPOUND

The present invention relates to UV absorber compositions, to the use of such compositions in protecting human and animal skin and hair from the harmful effects of UV radiation, and to their use in cosmetic and pharmaceutical formulations.

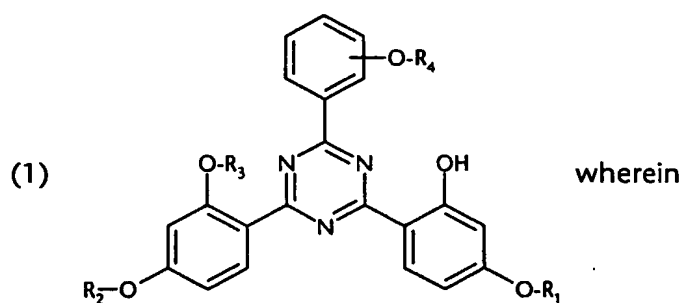
It is known that certain organic UV filters, such as, for example, poorly soluble triazine compounds, have pronounced UV filter properties. However, the solubility of such organic UV filters in solvents that are suitable for cosmetic formulations is often inadequate.

There is strong interest in organic light-protective filters that can be readily incorporated in cosmetic formulations, that is to say that have good oil-solubility.

The problem of the present invention is therefore to find organic UV filters or UV filter mixtures that have good solubility in solvents that are suitable for cosmetic formulations.

It has now been found, surprisingly, that UV absorber compositions comprising selected triazine compounds have such properties.

The present invention accordingly relates to a UV absorber composition comprising
(a) from 1 to 99 % by weight of a hydroxyphenyltriazine compound of formula



R₁, R₂ and R₃ are each independently of the others C₁-C₁₈alkyl; C₂-C₁₀alkenyl; or phenyl-C₁-C₄alkyl;

R₄ is hydrogen; or C₁-C₃alkyl; and

(b) from 99 to 1 % by weight of a further UV absorber selected from the group of

(b₁) hydroxyphenyltriazines that are different from component (a), (b₂) benzotriazoles,

(b₃) dibenzoylmethane derivatives and (b₄) camphor derivatives.

C₁-C₁₈Alkyl radicals are straight-chain or branched alkyl radicals such as, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, amyl, isoamyl or tert-amyl, heptyl, octyl, isooctyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl or octadecyl.

C₂-C₁₀Alkenyl is, for example, allyl, methallyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl or isododecenyl.

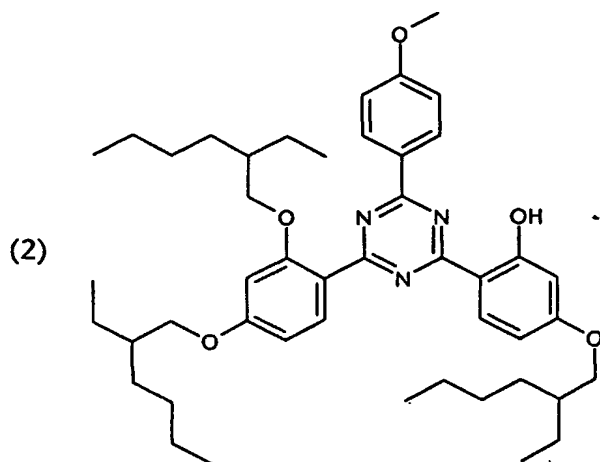
Phenyl-C₁-C₁₀alkyl is, for example, phenylbutyl, phenylpropyl, phenylethyl or, preferably, benzyl.

The composition preferably comprises
from 5 to 95 % of component (a) and
from 95 to 5 % of component (b).

In formula (1), R₁, R₂ and R₃ preferably are each independently of the others C₅-C₁₂alkyl.

R₁, R₂ and R₃ preferably have the same meaning.

Very special preference is given to a UV absorber composition wherein
component (a) corresponds to formula



Preference is further given to compounds of formula (I) wherein

R_1 and R_2 are C_5 - C_{12} alkyl;

R_3 is C_2 - C_{12} alkenyl, especially allyl; and

R_4 is hydrogen; or C_1 - C_3 alkyl.

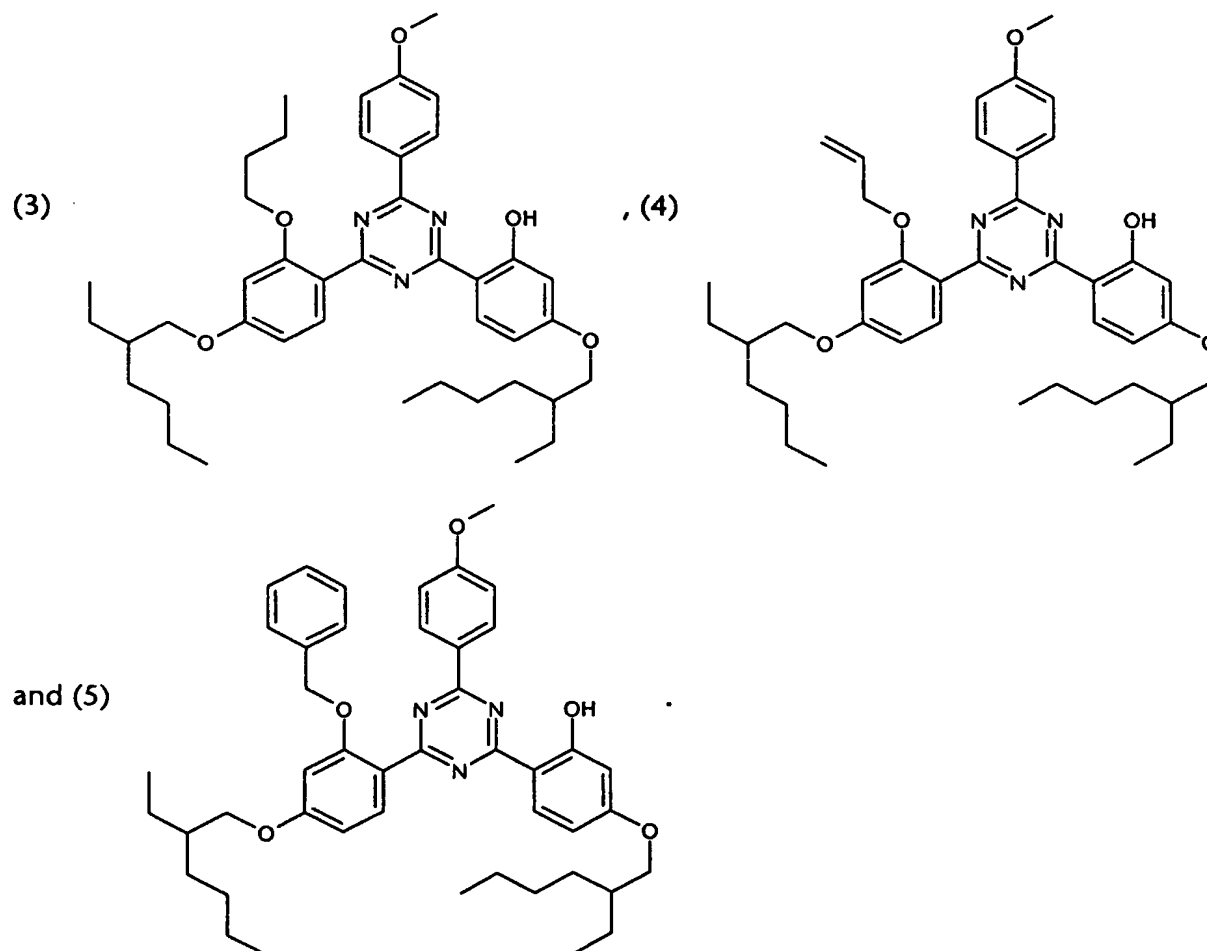
Preference is further given to compounds of formula (1) wherein

R_1 and R_2 are C_5 - C_{12} alkyl;

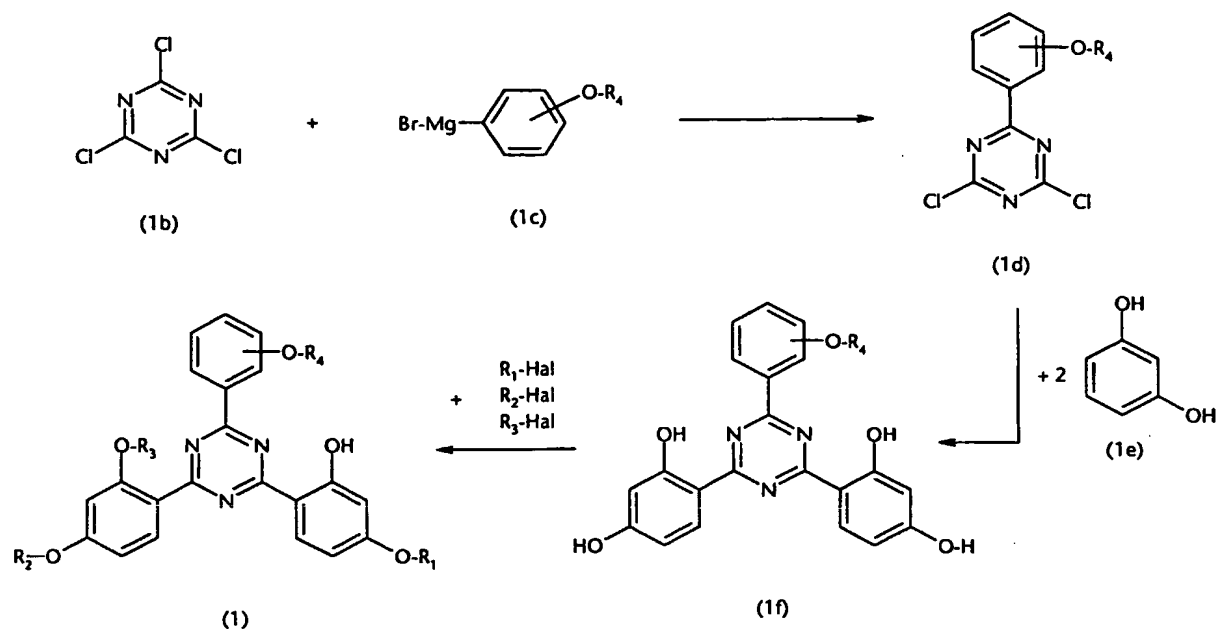
R_3 is phenyl; or phenyl- C_1 - C_4 alkyl; especially benzyl; and

R_4 is hydrogen; or C_1 - C_3 alkyl.

Examples of compounds used in accordance with the invention correspond to formulae



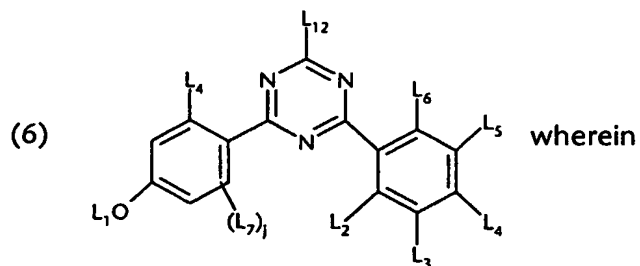
Preparation of the compounds of formula (1) is carried out in a manner known *per se* by reacting the appropriate phenylmagnesium bromide compound of formula (1c) in a Grignard reaction with cyanuric chloride (formula (1b)) to form the dichlorotriazine compound of formula (1d), introducing resorcinol groups by Friedel-Crafts acylation of resorcinol (formula (1e)) in the presence of a Lewis acid, especially aluminium chloride, and etherifying the free hydroxyl groups in the p- and o-positions of the compound of formula (1f), according to the meanings of the radicals R_1 , R_2 and R_3 , by alkylation to form the compound of formula (1), in accordance with the following scheme:



Details thereof can be found in the Preparation Examples.

The compounds of formula (1) are suitable as UV absorbers, especially as light-protective agents for human skin and hair.

Component (b) of the composition according to the invention preferably comprises a UV absorber of formula



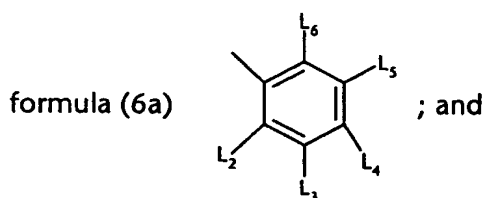
L_1 is C_1 - C_{22} alkyl, C_2 - C_{22} alkenyl or C_5 - C_7 cycloalkyl;

L_2 and L_6 are each independently of the other hydrogen, hydroxy, halogen, C_1 - C_{22} alkyl or halomethyl;

L_3 , L_5 and L_7 are each independently of the others hydrogen, hydroxy, OL_1 , halogen, C_1 - C_{22} alkyl or halomethyl;

L_4 is hydrogen, hydroxy, $-OL_1$, halogen, C_1 - C_{22} alkyl, phenyl or halomethyl;

L_{12} is C_1 - C_{22} alkyl, phenyl- C_1 - C_3 alkyl, C_5 - C_7 cycloalkyl, OL_1 or, preferably, a group of



j is 0, 1, 2 or 3.

C_2 - C_{22} Alkenyl is, for example, allyl, methallyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, isododecenyl, n-dodec-2-enyl or n-octadec-4-enyl.

C_5 - C_7 Cycloalkyl is cyclopentyl, cycloheptyl or, preferably, cyclohexyl.

Halogen is fluorine, bromine, iodine or, preferably, chlorine.

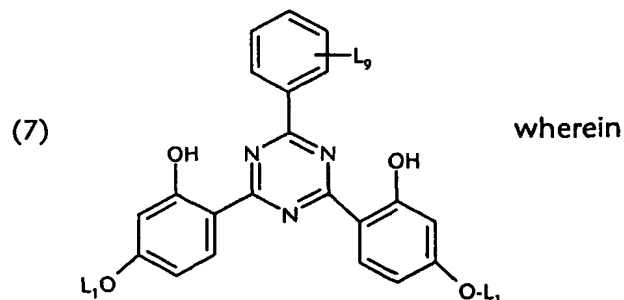
Very special preference is given, in accordance with the invention, to compounds of formula (6) wherein

L_1 is C_1 - C_{22} alkyl; C_2 - C_{22} alkenyl; or C_5 - C_7 cycloalkyl;

L_2 , L_3 , L_5 and L_7 are hydrogen; and

L_4 and L_6 are as defined for formula (6).

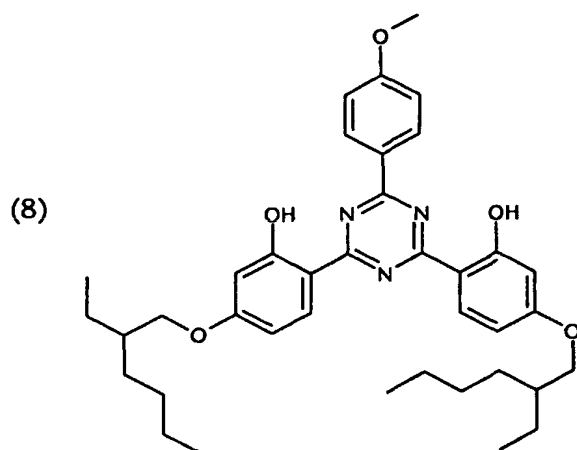
Very special preference is given to hydroxyphenyltriazine compounds of formula



L_1 is C_1 - C_{22} alkyl, C_2 - C_{22} alkenyl or C_3 - C_7 cycloalkyl; and

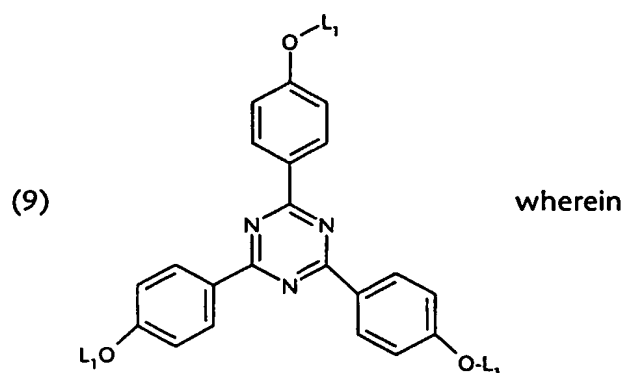
L_9 is C_1 - C_5 alkyl; or C_1 - C_5 alkoxy.

Very special preference is given to the use of the hydroxyphenyltriazine compound of formula



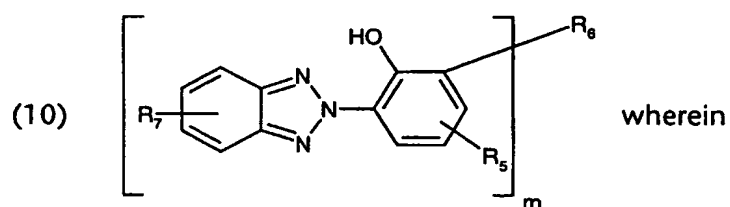
as component (b₁) in the composition according to the invention.

Further hydroxyphenyltriazine compounds of component (b₁) the use of which is preferred correspond to formula

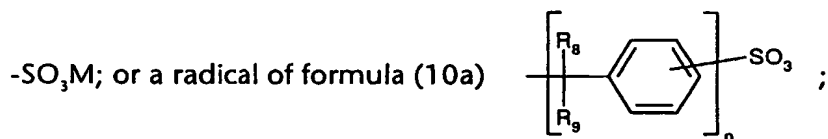


L_1 is C_1 - C_{22} alkyl; preferably C_1 - C_3 alkyl; and especially methyl.

Preference is also given to the use, as component (b₂), of benzotriazole compounds of formula



R_5 is C_1 - C_{12} alkyl; C_1 - C_3 alkoxy; C_1 - C_3 alkoxycarbonyl; C_5 - C_7 cycloalkyl; C_6 - C_{10} aryl; aralkyl;



R_7 is hydrogen; C_1 - C_3 alkyl; C_1 - C_3 alkoxy; halogen, preferably chlorine; or hydroxy;

R_8 and R_9 are each independently of the other hydrogen; or C_1 - C_3 alkyl;

m is 1 or 2;

n is 0 or 1;

when $m = 1$,

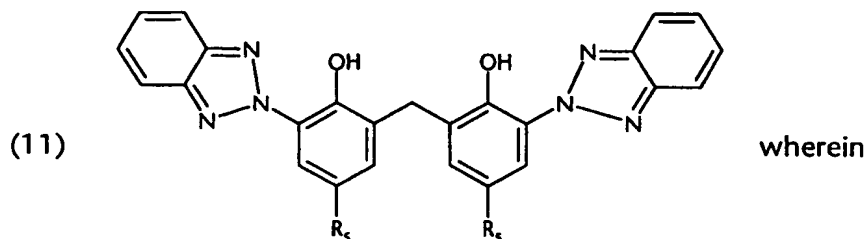
R_6 is hydrogen; unsubstituted or phenyl-substituted C_1 - C_{12} alkyl; or C_6 - C_{10} aryl;

when $m = 2$,

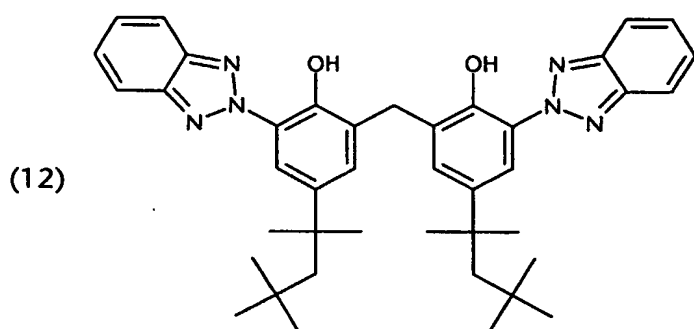
R_6 is a direct bond; or $-(CH_2)_p$ -; and

p is from 1 to 3.

Preferred benzotriazole compounds of component (b) suitable for use according to the invention correspond to formula



R_5 is C_1 - C_{12} alkyl, especially C_1 - C_8 alkyl; very especially the compound of formula



There is furthermore used, as component (b₃), preferably 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)propane-1,3-dione or butylmethoxydibenzoylmethane or, as component (b₄), a camphor derivative.

By virtue of its lipophilicity, the UV absorber composition according to the invention, on its own or together with other soluble organic UV absorbers, can readily be incorporated, in accordance with known methods, into oil- and fat-containing cosmetic formulations such as, for example, oils, O/W or W/O emulsions, fat-containing formulations in stick form, or gels.

The compounds of the formula (1) according to the present invention are particularly suitable as UV filters, i.e. for protecting ultraviolet-sensitive organic materials, in particular the skin and hair of humans and animals, from the harmful effects of UV radiation. These compounds are therefore suitable as sunscreens in cosmetic, pharmaceutical and veterinary medical preparations. These compounds can be used both in dissolved form and in the micronized state.

The UV absorbers according to the present invention can be used either in the dissolved state (soluble organic filters, solubilized organic filters) or in the micronised state (nanoscalar organic filters, particulate organic filters, UV-absorber pigments).

Any known process suitable for the preparation of microparticles can be used for the preparation of the micronised UV absorbers, for example:

- wet-milling (low viscous micronisation process for pump-able dispersions), with a hard grinding medium, for example zirconium silicate balls in a ball mill and a protective surfactant or a protective polymer in water or in a suitable organic solvent;
- wet-kneading (high viscosity micronisation process for non pump-able pastes) using a continuous or discontinuous (batch) kneader. For a wet-kneading process a solvent (water or cosmetically acceptable oils), a grinding-aid (surfactant, emulsifier) and a polymeric grinding aid may be used.
- spray-drying from a suitable solvent, for example aqueous suspensions or suspensions containing organic solvents, or true solutions in water, ethanol, dichloroethane, toluene or N-methylpyrrolidone etc..
- by the expansion according to the RESS process (Rapid Expansion of Supercritical Solutions) of supercritical fluids (e.g. CO₂) in which the UV filter or filters is/are dissolved, or the expansion of fluid carbon dioxide together with a solution of one or more UV filters in a suitable organic solvent;
- by reprecipitation from suitable solvents, including supercritical fluids (GASR process = Gas Anti-Solvent Recrystallisation / PCA process = Precipitation with Compressed Anti-solvents).

As milling apparatus for the preparation of the micronised organic UV absorbers there may be used, for example, a jet mill, ball mill, vibratory mill or hammer mill, preferably a high-speed mixing mill. Even more preferably mills are modern ball mills, manufacturers of these mill-types are for example Netzsch (LMZ-mill), Drais (DCP-viscoflow or cosmo), Bühler AG (centrifugal mills) or Bachhofer. The grinding is preferably carried out with a grinding aid.

As kneading apparatus for the preparation of the micronised organic UV absorbers examples are typical sigma-hook batch kneaders but also serial batch kneaders (IKA-Werke) or continuous kneaders (Continua from Werner und Pfleiderer).

Useful low molecular weight grinding aids for all the above micronizing processes are surfactants and emulsifiers as disclosed below in the chapters "emulsifiers" and "surfactants".

Useful polymeric grinding aids for water dispersion are cosmetically acceptable water soluble polymers for example: acrylates (Salcare types), modified or non-modified polysaccharides, polyglucosides or xanthan gum. Furthermore an alkylated vinylpyrrolidone polymer, a vinylpyrrolidone/vinyl acetate copolymer, an acyl glutamate, an alkyl polyglucoside, cetareth-25 or a phospholipid may be used. Oil dispersions may contain cosmetically acceptable waxy polymers or natural waxes as polymeric grinding aid to adjust viscosity during and after processing.

Useful solvents are water, brine, (poly-)ethylene glycol or glycerine for water-soluble dispersions and also cosmetically acceptable oils such as those described under "emollients" for oil-soluble dispersions.

The micronised UV absorbers so obtained usually have an average particle size from 0.02 to 2 micrometers, preferably from 0.05 to 1.5 micrometers and more especially from 0.1 to 1.0 micrometers.

The UV absorbers can also be used dry in powder form. For that purpose the UV absorbers are subjected to known grinding methods, such as vacuum atomization, countercurrent spray-drying etc.. Such powders have a particle size of from 0.1 micrometer to 2 micrometers. To avoid the occurrence of agglomeration, the UV absorbers can be coated with a surface-active compound prior to the pulverisation process, for example with an anionic, non-ionic or amphoteric surfactant, e.g. a phospholipid or a known polymer, such as PVP, an acrylate etc.

The cosmetic formulations or pharmaceutical compositions according to the present invention can also contain one or more than one further UV filter as described in table 1–3.

The cosmetic or pharmaceutical preparations can be prepared by physically mixing the UV absorber(s) with the adjuvant using customary methods, for example by simply stirring together the individual components, especially by making use of the dissolution properties of already known cosmetic UV absorbers, for example octyl methoxy cinnamate, salicylic acid isooctyl ester, etc. The UV absorber can be used, for example, without further treatment, or in the micronised state, or in the form of a powder.

Cosmetic or pharmaceutical preparations contain from 0.05-40% by weight, based on the total weight of the composition, of one UV absorber or UV absorber mixtures.

Preference is given to the use of mixing ratios of the UV absorber of formula (1) according to the invention and optionally further light-protective agents (as described in table 1-3) from 1:99 to 99:1, especially from 1:95 to 95:1 and preferably from 10:90 to 90:10, based on weight. Of special interest are mixing ratios of from 20:80 to 80:20, especially from 40:60 to 60:40 and preferably approximately 50:50. Such mixtures can be used, *inter alia*, to improve solubility or increase UV absorption.

The UV absorbers of formula (1) according to the present invention or combinations of UV filters are useful for the protection of skin, hair and/or natural or artificial hair color.

Table 1. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention

p-aminobenzoic acid derivatives, for example 4-dimethylaminobenzoic acid 2-ethylhexyl ester;
salicylic acid derivatives, for example salicylic acid 2-ethylhexyl ester;
benzophenone derivatives, for example 2-hydroxy-4-methoxybenzophenone and its 5-sulfonic acid derivative;
dibenzoylmethane derivatives, for example 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione;
diphenylacrylates, for example 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, and 3-(benzofuran-yl) 2-cyanoacrylate;
3-imidazol-4-ylacrylic acid and esters;
benzofuran derivatives, especially 2-(p-aminophenyl)benzofuran derivatives, described in EP-A-582 189, US-A-5 338 539, US-A-5 518 713 and EP-A-613 893;
polymeric UV absorbers, for example the benzylidene malonate derivatives described in EP-A-709 080;
cinnamic acid derivatives, for example the 4-methoxycinnamic acid 2-ethylhexyl ester and isoamyl ester or cinnamic acid derivatives described in US-A-5 601 811 and WO 97/00851;
camphor derivatives, for example 3-(4'-methyl)benzylidene-bornan-2-one, 3-benzylidene-bornan-2-one, N-[2(and 4)-2-oxyborn-3-ylidene-methyl]-benzyl]acrylamide polymer, 3-(4'-trimethylammonium)-benzylidene-bornan-2-one methyl sulfate, 3,3'-(1,4-phenylenedimethine)-bis(7,7-dimethyl-2-oxo-bicyclo[2.2.1]heptane-1-methanesulfonic acid) and salts, 3-(4'-sulfo)benzylidene-bornan-2-one and salts; camphorbenzalkonium methosulfate;
hydroxyphenyltriazine compounds, for example 2-(4'-methoxyphenyl)-4,6-bis(2'-hydroxy-4'-n-octyloxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-

hydroxy]-phenyl)-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(2-ethyl-hexyloxy)-2-hydroxy]-phenyl]-6-[4-(2-methoxyethyl-carboxyl)-phenylamino]-1,3,5-triazine; 2,4-bis[[4-(tris(trimethylsilyloxy-silyl)propyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(2"-methylpropenyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(1',1',1',3',5',5',5'-heptamethyltrisilyl-2"-methyl-propyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-hydroxy]-phenyl]-6-[4-ethylcarboxy]-phenylamino]-1,3,5-triazine;
benzotriazole compounds, for example 2,2'-methylene-bis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol;
trianilino-s-triazine derivatives, for example 2,4,6-trianiline-(p-carbo-2'-ethyl-1'-oxy)-1,3,5-triazine and the UV absorbers disclosed in US-A-5 332 568, EP-A-517 104, EP-A-507 691, WO 93/17002 and EP-A-570 838;
2-phenylbenzimidazole-5-sulfonic acid and salts thereof;
menthyl o-aminobenzoates;
physical sunscreens coated or not coated, such as titanium dioxide, zinc oxide, iron oxides, mica, MnO, Fe ₂ O ₃ , Ce ₂ O ₃ , Al ₂ O ₃ , ZrO ₂ . (surface coatings: polymethylmethacrylate, methicone (methylhydrogenpolysiloxane as described in CAS 9004-73-3), dimethicone, isopropyl titanium triisostearate (as described in CAS 61417-49-0), metal soaps such as magnesium stearate (as described in CAS 4086-70-8), perfluoroalcohol phosphate as C9-15 fluoroalcohol phosphate (as described in CAS 74499-44-8; JP 5-86984 , JP 4-330007)). The primary particle size is an average of 15nm–35nm and the particle size in dispersion is in the range of 100nm – 300nm.
aminohydroxy-benzophenone derivatives disclosed in DE 10011317, EP 1133980 and EP 1046391
phenyl-benzimidazole derivatives as disclosed in EP 1167358
the UV absorbers described in "Sunscreens", Eds. N.J. Lowe, N.A.Shaath, Marcel Dekker, Inc., New York and Basle or in Cosmetics & Toiletries (107), 50ff (1992) also can be used as additional UV protective substances.

Table 2. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention are described in the following patents; (preferred are the compounds in the 2nd column)

(Abbreviations T: table, R: row, Comp: compound, Ex: compound(s) of patent example, p: page)

DE 100331804	Tab 1 p 4, tab 2 + 3 p 5
EP 613893	Ex 1-5 + 15, T 1, pp 6-8
EP 1000950	Comp. in table 1, pp 18-21
EP 1005855	T 3, p 13
EP 1008586	Ex 1-3, pp 13-15
EP 1008593	Ex 1-8, pp 4-5
EP 1027883	Compound VII, p 3
EP 1027883	Comp I-VI, p 3

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EP 1028120	Ex 1-5, pp 5-13
EP 1059082	Ex 1; T 1, pp 9-11
EP 1060734	T 1-3, pp 11-14
EP 1064922	Compounds 1-34, pp 6-14
EP 1081140	Ex 1-9, pp 11-16
EP 1103549	Compounds 1-76, pp 39-51
EP 1108712	4,5-Dimorpholino-3-hydroxypyridazine
EP 1123934	T 3, p 10
EP 1129695	Ex 1-7, pp 13-14
EP 1167359	Ex 1 p11 and ex 2 p 12
EP 420707 B1	Ex 3, p 13 (CAS Regno No. 80142-49-0)
EP 503338	T 1, pp 9-10
EP 517103	Ex 3,4,9,10 pp 6-7
EP 517104	Ex 1, T 1, pp 4-5; Ex 8, T 2, pp 6-8
EP 626950	all compounds
EP 669323	Ex 1-3, p 5
EP 780382	Ex 1-11, pp 5-7
EP 823418	Ex 1-4, pp 7-8
EP 826361	T 1, pp 5-6
EP 832641	Ex 5+6 p 7; t 2, p 8
EP 832642	Ex 22, T 3 pp, 10-15; T 4, p 16
EP 852137	T 2, pp 41-46
EP 858318	T 1, p 6
EP 863145	Ex 1-11, pp 12-18
EP 895776	Comp. in rows 48-58, p 3; R 25+33, p 5
EP 911020	T 2, p 11-12
EP 916335	T 2-4, pp 19-41
EP 924246	T 2, p 9

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(Abbreviations T: table, R: row, Comp: compound, Ex: compound(s) of patent example, p: page)

EP 933376	Ex 1-15, pp 10-21
EP 944624	Ex 1+2, pp13-15
EP 945125	T 3 a+b, pp 14-15
EP 967200	Ex 2; T 3-5, pp 17-20
EP 969004	Ex 5, T 1, pp 6-8
JP 2000319629	CAS Reg. No. 80142-49-0, 137215-83-9, 307947-82-6
US 5635343	all compounds on pp 5-10
US 5338539	Ex 1-9, pp 3+4
US 5346691	Ex 40, p 7; T 5, p 8
US 5801244	Ex 1-5, pp 6-7
WO 0149686	Ex 1-5, pp 16-21
WO 0168047	Tables on pp 85-96
WO 0181297	Ex 1-3 pp 9-11
WO 0238537	All compounds p 3, compounds on rows 1-10 p 4
WO 9217461	Ex 1-22, pp 10-20
WO 9220690	Polymeric comp in examples 3-6
WO 9301164	T 1+2, pp 13-22
WO 9714680	Ex 1-3, p 10

Table 3. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention

No.	Chemical Name	CAS No.
1	(+/-)-1,7,7-trimethyl-3-[(4-methylphenyl)methylene]bicyclo-[2.2.1]heptan-2-one	36861-47-9
2	1,7,7-trimethyl-3-(phenylmethylene)bicyclo[2.2.1]heptan-2-one	15087-24-8
3	(2-Hydroxy-4-methoxyphenyl)(4-methylphenyl)methanone	1641-17-4
4	2,4-dihydroxybenzophenone	131-56-6
5	2,2',4,4'-tetrahydroxybenzophenone	131-55-5
6	2-Hydroxy-4-methoxy benzophenone;	131-57-7

Table 3. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention

7	2-Hydroxy-4-methoxy benzophenone-5-sulfonic acid	4065-45-6
8	2,2'-dihydroxy-4,4'-dimethoxybenzophenone	131-54-4
9	2,2'-Dihydroxy-4-methoxybenzophenone	131-53-3
10	Alpha-(2-oxoborn-3-ylidene)toluene-4-sulphonic acid and its salts	56039-58-8
11	1-[4-(1,1-dimethylethyl)phenyl]-3-(4-methoxyphenyl)propane-1,3-dione	70356-09-1
12	Methyl N,N,N-trimethyl-4-[(4,7,7-trimethyl-3-oxobicyclo[2,2,1]hept-2-ylidene)methyl]anilinium sulphate;	52793-97-2
22	3,3,5-Trimethyl cyclohexyl-2-hydroxy benzoate	118-56-9
23	Isopentyl p-methoxycinnamate	71617-10-2
27	Menthyl-o-aminobenzoate	134-09-8
28	Menthyl salicylate	89-46-3
29	2-Ethylhexyl 2-cyano,3,3-diphenylacrylate	6197-30-4
30	2- ethylhexyl 4- (dimethylamino)benzoate	21245-02-3
31	2- ethylhexyl 4- methoxycinnamate	5466-77-3
32	2- ethylhexyl salicylate	118-60-5
33	Benzoic acid, 4, 4', 4''- (1, 3, 5- triazine- 2, 4, 6- triyltriimino)tris-, tris(2- ethylhexyl) ester; 2,4,6-Trianilino-(p-carbo-2'-ethylhexyl-1'-oxi)-1,3,5-triazine	88122-99-0
34	4- aminobenzoic acid	150-13-0
35	Benzoic acid, 4-amino-, ethyl ester, polymer with oxirane	113010-52-9
38	2- phenyl- 1H- benzimidazole- 5- sulphonic acid	27503-81-7
39	2-Propenamide, N-[[4-[(4,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-2-ylidene)methyl]phenyl]methyl]-, homopolymer	147897-12-9
40	Triethanolamine salicylate	2174-16-5
41	3, 3'- (1, 4- phenylenedimethylene)bis[7, 7- dimethyl- 2- oxo-bicyclo[2.2.1]heptane- 1- methanesulfonic acid]	90457-82-2
42	Titanium dioxide	13463-67-7
44	Zinc oxide	1314-13-2
45	2,2'-Methylene-bis-[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol]	103597-45-1
46	2,4-bis[[4-(2-ethylhexyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-(1,3,5)-triazine	187393-00-6
47	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt	180898-37-7
48	Benzoic acid, 4,4'-[[6-[[4-[[[(1,1-dimethylethyl)amino]carbonyl]phenyl]amino]1,3,5-triazine-2,4-	154702-15-5

Table 3. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention		
	dimethylethyl)amino]carbonyl]phenyl]amino]1,3,5-triazine-2,4-diyl]diimino]bis-, bis(2-ethylhexyl)ester	
49	Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl]-	155633-54-8
50	alpha-(trimethylsilyl)-omega-(trimethyl-silyloxy)poly[oxy(dimethyl-silylene)-co-[oxy(methyl)(2-{p-[2,2-bis(ethoxycarbonyl)vinyl]-phenoxy}-1 methyleneethyl)silylene]-co-[oxy(methyl)(2-{p-[2,2-bis(ethoxycarbonyl)vinyl]phenoxy}prop-1-enyl)silylene]	207574-74-1
51	Benzenesulfonic acid, 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)-, monosodium salt	92484-48-5
52	Benzoic acid, 2-[4-(diethylamino)-2-hydroxybenzoyl]-, hexyl ester	302776-68-7
53	1-Dodecanaminium, N-[3-[[4-(dimethylamino)benzoyl]amino]-propyl]N,N-dimethyl-, salt with 4-methylbenzenesulfonic acid (1:1)	156679-41-3
54	1-Propanaminium, N,N,N-trimethyl-3-[(1-oxo-3-phenyl-2-propenyl)amino]-, chloride	177190-98-6
55	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-	170864-82-1
56	1,3,5-Triazine, 2,4,6-tris(4-methoxyphenyl)-	7753-12-0
57	1,3,5-Triazine, 2,4,6-tris[4-[(2-ethylhexyl)oxy]phenyl]-	208114-14-1
58	1-Propanaminium, 3-[[3-[3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]amino]-N,N-diethyl-N-methyl-, methyl sulfate (salt)	340964-15-0
59	2-Propenoic acid, 3-(1H-imidazol-4-yl)-	104-98-3
60	Benzoic acid, 2-hydroxy-, [4-(1-methylethyl)phenyl]methyl ester	94134-93-7
61	1,2,3-Propanetriol, 1-(4-aminobenzoate)	136-44-7
62	Benzeneacetic acid, 3,4-dimethoxy-a-oxo-	4732-70-1
63	2-Propenoic acid, 2-cyano-3,3-diphenyl-, ethyl ester	5232-99-5

Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention are any UV-A and UV-B filter substances.

The cosmetic or pharmaceutical preparations may be, for example, creams, gels, lotions, alcoholic and aqueous/alcoholic solutions, emulsions, wax/fat compositions, stick preparations, powders or ointments. In addition to the above mentioned UV filters, the cosmetic or pharmaceutical preparations may contain further adjuvants as described below.

As water- and oil-containing emulsions (e.g. W/O, O/W, O/W/O and W/O/W emulsions or microemulsions) the preparations contain, for example, from 0.1 to 30 % by weight, pre-

ferably from 0.1 to 15 % by weight and especially from 0.5 to 10 % by weight, based on the total weight of the composition, of one or more UV absorbers, from 1 to 60 % by weight, especially from 5 to 50 % by weight and preferably from 10 to 35 % by weight, based on the total weight of the composition, of at least one oil component, from 0 to 30 % by weight, especially from 1 to 30 % by weight and preferably from 4 to 20 % by weight, based on the total weight of the composition, of at least one emulsifier, from 10 to 90 % by weight, especially from 30 to 90 % by weight, based on the total weight of the composition, of water, and from 0 to 88.9 % by weight, especially from 1 to 50 % by weight, of further cosmetically acceptable adjuvants.

The cosmetic or pharmaceutical compositions/preparations according to the invention may also contain one or one more additional compounds as described below.

Fatty alcohols

Guerbet alcohols based on fatty alcohols having from 6 to 18, preferably from 8 to 10 carbon atoms including cetyl alcohol, stearyl alcohol, cetearyl alcohol, oleyl alcohol, octyldodecanol, benzoate of C12-C15 alcohols, acetylated lanolin alcohol, etc..

Esters of fatty acids

Esters of linear C_6 - C_{24} fatty acids with linear C_3 - C_{24} alcohols, esters of branched C_8 - C_{13} carboxylic acids with linear C_6 - C_{24} fatty alcohols, esters of linear C_6 - C_{24} fatty acids with branched alcohols, especially 2-ethylhexanol, esters of hydroxycarboxylic acids with linear or branched C_6 - C_{22} fatty alcohols, especially dioctyl malates, esters of linear and/or branched fatty acids with polyhydric alcohols (for example propylene glycol, dimer diol or trimer triol) and/or Guerbet alcohols, for example caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselinic acid, linoleic acid, linolenic acid, elaeostearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid and technical-grade mixtures thereof (obtained, for example, in the pressure removal of natural fats and oils, in the reduction of aldehydes from Roelen's oxosynthesis or in the dimerisation of unsaturated fatty acids) with alcohols, for example, isopropyl alcohol, caproic alcohol, capryl alcohol, 2-ethylhexyl alcohol, capric alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol,

petroselinyl alcohol, linoyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachidyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol and technical-grade mixtures thereof (obtained, for example, in the high-pressure hydrogenation of technical-grade methyl esters based on fats and oils or aldehydes from Roelen's oxosynthesis and as monomer fractions in the dimerisation of unsaturated fatty alcohols).

Examples of such ester oils are isopropyl myristate, isopropyl palmitate, isopropyl stearate, isopropyl isostearate, isopropyl oleate, n-butyl stearate, n-hexyl laurate, n-decyl oleate, iso-octyl stearate, iso-nonyl stearate, isononyl isononanoate, 2-ethylhexyl palmitate, 2-hexyl laurate, 2-hexyldecyl stearate, 2-octyldodecyl palmitate, oleyl oleate, oleyl erucate, erucyl oleate, erucyl erucate, cetearyl octanoate, cetyl palmitate, cetyl stearate, cetyl oleate, cetyl behenate, cetyl acetate, myristyl myristate, myristyl behenate, myristyl oleate, myristyl stearate, myristyl palmitate, myristyl lactate, propylene glycol dicaprylate/caprates, stearyl heptanoate, diisostearyl malate, octyl hydroxystearate, etc..

Other adjuvants

diethylhexyl 2,6-naphthalate, di-n-butyl adipate, di(2-ethylhexyl)-adipate, di(2-ethylhexyl)-succinate and diisotridecyl acetate, and also diol esters, such as ethylene glycol dioleate, ethylene glycol diisotridecanoate, propylene glycol di(2-ethylhexanoate), propylene glycol diisostearate, propylene glycol dipelargonate, butanediol diisostearate and neopentyl glycol dicaprylate. Esters of C_6 - C_{24} fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, saturated and/or unsaturated, especially benzoic acid, esters of C_2 - C_{12} dicarboxylic acids with linear or branched alcohols having from 1 to 22 carbon atoms or polyols having from 2 to 10 carbon atoms and from 2 to 6 hydroxy groups.

Natural or synthetic triglycerides including glyceryl esters and derivatives

Di- or tri-glycerides, based on C_6 - C_{18} fatty acids, modified by reaction with other alcohols (caprylic/capric triglyceride, wheat germ glycerides, etc.). Fatty acid esters of polyglycerin (polyglyceryl-n such as polyglyceryl-4 caprate, polyglyceryl-2 isostearate, etc. or castor oil, hydrogenated vegetable oil, sweet almond oil, wheat germ oil, sesame oil, hydrogenated cottonseed oil, coconut oil, avocado oil, corn oil, hydrogenated castor oil, shea butter, cocoa butter, soybean oil, mink oil, sunflower oil, safflower oil, macadamia nut oil, olive oil, hydrogenated tallow, apricot kernel oil, hazelnut oil, borago oil, etc.

Waxes including esters of long-chain acids and alcohols as well as compounds having wax-like properties, e.g., carnauba wax, beeswax (white or yellow), lanolin wax, candellila wax, ozokerite, japan wax, paraffin wax, microcrystalline wax, ceresin, cetearyl esters wax, synthetic beeswax, etc.. Also, hydrophilic waxes as cetearyl alcohol or partial glycerides.

Pearlescent waxes:

Alkylene glycol esters, especially ethylene glycol distearate; fatty acid alkanolamides, especially coco fatty acid diethanolamide; partial glycerides, especially stearic acid monoglyceride; esters of polyvalent, unsubstituted or hydroxy-substituted carboxylic acids with fatty alcohols having from 6 to 22 carbon atoms, especially long-chained esters of tartaric acid; fatty substances, for example fatty alcohols, fatty ketones, fatty aldehydes, fatty ethers and fatty carbonates, which in total have at least 24 carbon atoms, especially laurone and distearyl ether; fatty acids, such as stearic acid, hydroxystearic acid or behenic acid, ring-opening products of olefin epoxides having from 12 to 22 carbon atoms with fatty alcohols having from 12 to 22 carbon atoms and/or polyols having from 2 to 15 carbon atoms and from 2 to 10 hydroxy groups, and mixtures thereof.

Hydrocarbon oils:

Mineral oil (light or heavy), petrolatum (yellow or white), microcrystalline wax, paraffinic and isoparaffinic compounds, hydrogenated isoparaffinic molecules as polydecenes and polybutene, hydrogenated polyisobutene, squalane, isohexadecane, isododecane and others from plant and animal kingdom.

Silicones or siloxanes (organosubstituted polysiloxanes)

Dimethylpolysiloxanes, methylphenylpolysiloxanes, cyclic silicones, and also amino-, fatty acid-, alcohol-, polyether-, epoxy-, fluorine-, glycoside- and/or alkyl-modified silicone compounds, which at room temperature may be in either liquid or resinous form. Linear polysiloxanes, dimethicone (Dow Corning 200 fluid, Rhodia Mirasil DM), dimethiconol, cyclic silicone fluids, cyclopentasiloxanes volatiles (Dow Corning 345 fluid), phenyltrimethicone (Dow Corning 556 fluid). Also suitable are simethicones, which are mixtures of dimethicones having an average chain length of from 200 to 300 dimethylsiloxane units with hydroge-

nated silicates. A detailed survey by Todd *et al.* of suitable volatile silicones may in addition be found in Cosm. Toil. 91, 27 (1976).

Fluorinated or perfluorinated oils

Perfluorohexane, dimethylcyclohexane, ethylcyclopentane, polyperfluoromethylisopropyl ether.

Emulsifiers

Any conventionally usable emulsifier can be used for the compositions. Emulsifier systems may comprise for example: carboxylic acids and their salts: alkaline soap of sodium, potassium and ammonium, metallic soap of calcium or magnesium, organic basis soap such as lauric, palmitic, stearic and oleic acid etc.. Alkyl phosphates or phosphoric acid esters, acid phosphate, diethanolamine phosphate, potassium cetyl phosphate. Ethoxylated carboxylic acids or polyethylene glycol esters, PEG-n acylates. Linear fatty alcohols having from 8 to 22 carbon atoms, branched from 2 to 30 mol of ethylene oxide and/or from 0 to 5 mol propylene oxide with fatty acids having from 12 to 22 carbon atoms and with alkylphenols having from 8 to 15 carbon atoms in the alkyl group. Fatty alcohol polyglycol ethers such as laureth-n, cetareth-n, steareth-n, oleth-n. Fatty acid polyglycoether such as PEG-n stearate, PEG-n oleate, PEG-n cocoate. Monoglycerides and polyol esters. C₁₂-C₂₂ fatty acid mono- and diesters of addition products of from 1 to 30 mol of ethylene oxide with polyols. Fatty acid and polyglycerol ester such as monostearate glycerol, diisostearoyl polyglyceryl-3-diisostearates, polyglyceryl-3-diisostearates, triglyceryl diisostearates, polyglyceryl-2-sesquiisostearates or polyglyceryl dimerates. Mixtures of compounds from a plurality of those substance classes are also suitable. Fatty acid polyglycolesters such as monostearate diethylene glycol, fatty acid and polyethylene glycol esters, fatty acid and saccharose esters such as sucro esters, glycerol and saccharose esters such as sucro glycerides. Sorbitol and sorbitan, sorbitan mono- and di-esters of saturated and unsaturated fatty acids having from 6 to 22 carbon atoms and ethylene oxide addition products. Polysorbate-n series, sorbitan esters such as sesquiisostearate, sorbitan, PEG-(6)-isostearate sorbitan, PEG-(10)-sorbitan laurate, PEG-17-dioleate sorbitan. Glucose derivatives, C₈-C₂₂ alkyl-mono and oligo-glycosides and ethoxylated analogues with glucose being preferred as the sugar component. O/W emulsifiers such as methyl gluceth-20 sesquisteate, sorbitan stearate/sucrose cocoate, methyl glucose sesquisteate, cetearyl alcohol/cetearyl glucoside. W/O emulsifiers such as methyl glucose

dioleate/ methyl glucose isostearate. Sulfates and sulfonated derivatives, dialkylsulfo-succinates, dioctyl succinate, alkyl lauryl sulfonate, linear sulfonated paraffins, sulfonated tetrapropylene sulfonate, sodium lauryl sulfates, ammonium and ethanolamine lauryl sulfates, lauryl ether sulfates, sodium laureth sulfates, sulfosuccinates, acetyl isothionates, alkanolamide sulfates, taurines, methyl taurines, imidazole sulfates. Amine derivatives, amine salts, ethoxylated amines, oxide amine with chains containing an heterocycle such as alkyl imidazolines, pyridine derivatives, isoquinoteines, cetyl pyridinium chloride, cetyl pyridinium bromide, quaternary ammonium such as cetyltrimethylbromide ammonium bromide (CTBA), stearylalkonium. Amide derivatives, alkanolamides such as acylamide DEA, ethoxylated amides such as PEG-n acylamide, oxydamide. Polysiloxane/polyalkyl/polyether copolymers and derivatives, dimethicone, copolyols, silicone polyethylene oxide copolymer, silicone glycol copolymer. Propoxylated or POE-n ethers (Meroxapols), poloxamers or poly(oxyethylene)m-block-poly(oxypropylene)n-block(oxyethylene). Zwitterionic surfactants that carry at least one quaternary ammonium group and at least one carboxylate and/or sulfonate group in the molecule. Zwitterionic surfactants that are especially suitable are betaines, such as N-alkyl-N,N-dimethylammonium glycinate, cocoalkyldimethylammonium glycinate, N-acylaminopropyl-N,N-dimethylammonium glycinate, cocoacylaminopropyl-dimethylammonium glycinate and 2-alkyl-3-carboxymethyl-3-hydroxyethylimidazolines each having from 8 to 18 carbon atoms in the alkyl or acyl group and also cocoacylaminoethyl-hydroxyethylcarboxymethylglycinate, N-alkylbetaine, N-alkylaminobetaines. Alkyl-imidazolines, alkylopeptides, lipoaminoacids, self-emulsifying bases and the compounds as described in K.F.DePolo, A short textbook of cosmetology, Chapter 8, Table 8-7, p250-251.

Non ionic bases such as PEG-6 beeswax (and) PEG-6 stearate (and) polyglyceryl -2-iso-stearate [Apifac], glyceryl stearate (and) PEG-100 stearate. [Arlacel 165], PEG-5 glyceryl stearate [Arlatone 983 S], sorbitan oleate (and) polyglyceryl-3 ricinoleate.[Arlacel 1689], sorbitan stearate and sucrose cocoate [Arlatone 2121], glyceryl stearate and laureth-23 [Cera-synth 945], cetearyl alcohol and ceteth-20 [Cetomacrogol Wax], cetearyl alcohol and polysorbate 60 and PEG-150 and stearate-20[Polawax GP 200, Polawax NF], cetearyl alcohol and cetearyl polyglucoside [Emulgade PL 1618], cetearyl alcohol and cetareth-20 [Emulgade 1000NI, Cosmowax], cetearyl alcohol and PEG-40 castor oil [Emulgade F Special], cetearyl alcohol and PEG-40 castor oil and sodium cetearyl sulfate [Emulgade F], stearyl alcohol and steareth-7 and steareth-10 [Emulgator E 2155], cetearyl alcohol and steareth-7 and steareth-

10 [Emulsifying wax U.S.N.F], glyceryl stearate and PEG-75 stearate [Gelot 64], propylene glycol ceteth-3 acetate [Hetester PCS], propylene glycol isoceth-3 acetate [Hetester PHA], cetearyl alcohol and ceteth-12 and oleth-12 [Lanbriol Wax N 21], PEG -6 stearate and PEG-32 stearate [Tefose 1500], PEG-6 stearate and ceteth-20 and steareth-20 [Tefose 2000], PEG-6 stearate and ceteth-20 and glyceryl stearate and steareth-20 [Tefose 2561], glyceryl stearate and cetareth-20 [Teginacid H, C, X].

Anionic alkaline bases such as PEG-2 stearate SE, glyceryl stearate SE [Monelgine, Cutina KD], propylene glycol stearate [Tegin P]. Anionic acid bases such as cetearyl alcohol and sodium cetearyl sulfate [Lanette N, Cutina LE, Crodacol GP], cetearyl alcohol and sodium lauryl sulfate [Lanette W], trilaneth-4 phosphate and glycol stearate and PEG-2 stearate [Sedefos 75], glyceryl stearate and sodium lauryl Sulfate [Teginacid Special]. Cationic acid bases such as cetearyl alcohol and cetrimonium bromide.

The emulsifiers may be used in an amount of, for example, from 1 to 30 % by weight, especially from 4 to 20 % by weight and preferably from 5 to 10 % by weight, based on the total weight of the composition.

When formulated in O/W emulsions, the preferred amount of such emulsifier system could represent 5% to 20% of the oil phase.

Adjuvants and additives

The cosmetic / pharmaceutical preparations, for example creams, gels, lotions, alcoholic and aqueous/alcoholic solutions, emulsions, wax/fat compositions, stick preparations, powders or ointments, may in addition contain, as further adjuvants and additives, mild surfactants, super-fattening agents, consistency regulators, thickeners, polymers, stabilisers, biogenic active ingredients, deodorising active ingredients, anti-dandruff agents, film formers, swelling agents, further UV light-protective factors, antioxidants, hydrotropic agents, preservatives, insect repellents, self-tanning agents, solubilisers, perfume oils, colourants, bacteria-inhibiting agents and the like.

Super-fatting agents

Substances suitable for use as super-fatting agents are, for example, lanolin and lecithin and also polyethoxylated or acrylated lanolin and lecithin derivatives, polyol fatty acid esters, monoglycerides and fatty acid alkanolamides, the latter simultaneously acting as foam stabilisers.

Surfactants

Examples of suitable mild surfactants, that is to say surfactants especially well tolerated by the skin, include fatty alcohol polyglycol ether sulfates, monoglyceride sulfates, mono- and/or di-alkyl sulfosuccinates, fatty acid isethionates, fatty acid sarcosinates, fatty acid tau-rides, fatty acid glutamates, α -olefin sulfonates, ethercarboxylic acids, alkyl oligoglucosides, fatty acid glucamides, alkylamidobetaines and/or protein fatty acid condensation products, the latter preferably being based on wheat proteins.

Consistency regulators/thickeners and rheology modifiers

Silicon dioxide, magnesium silicates, aluminium silicates, polysaccharides or derivatives thereof for example hyaluronic acid, xanthan gum, guar-guar, agar-agar, alginates, carrageenan, gellan, pectins, or modified cellulose such as hydroxycellulose, hydroxypropyl-methylcellulose. In addition polyacrylates or homopolymers of reticulated acrylic acids and polyacrylamides, carbomer (carbopol types 980, 981, 1382, ETD 2001, ETD2020, Ultrez 10) or Salcare range such as Salcare SC80(steareth-10 allyl ether/acrylates copolymer), Salcare SC81(acrylates copolymer), Salcare SC91 and Salcare AST(sodium acrylates copolymer/PPG-1 trideceth-6), Sepigel 305(polyacrylamide/laureth-7), Simulgel NS and Simulgel EG (hydroxyethyl acrylate / sodium acryloyldimethyl taurate copolymer), Stablen 30 (acrylates / vinyl isodecanoate crosspolymer), Pemulen TR-1(acrylates / C10-30 alkyl acrylate crosspolymer), Luvigel EM (sodium acrylates copolymer), Aculyn 28 (acrylates/beheneth-25 methacrylate copolymer), etc.

Polymers

Suitable cationic polymers are, for example, cationic cellulose derivatives, for example a quaternised hydroxymethyl cellulose obtainable under the name Polymer JR 400 from Amerchol, cationic starches, copolymers of diallylammonium salts and acrylamides, quaternised vinylpyrrolidone/vinyl imidazole polymers, for example Luviquat® (BASF), condensation

products of polyglycols and amines, quaternised collagen polypeptides, for example lauryl-dimonium hydroxypropyl hydrolyzed collagen (Lamequat®L/Grünau), quaternised wheat polypeptides, polyethyleneimine, cationic silicone polymers, for example amidomethicones, copolymers of adipic acid and dimethylaminohydroxypropyldiethylenetriamine (Carta-retin/Sandoz), copolymers of acrylic acid with dimethyldiallylammonium chloride (Merquat 550 / Chemviron), polyaminopolyamides, as described, for example, in FR-A-2 252 840, and the crosslinked water-soluble polymers thereof, cationic chitin derivatives, for example of quaternised chitosan, optionally distributed as microcrystals; condensation products of di-haloalkyls, for example dibromobutane, with bisdialkylamines, for example bisdimethyl-amino-1,3-propane, cationic guar gum, for example Jaguar C-17, Jaguar C-16 from Celanese, quaternised ammonium salt polymers, for example Mirapol A-15, Mirapol AD-1, Mirapol AZ-1 from Miranol. As anionic, zwitterionic, amphoteric and non-ionic polymers there come into consideration, for example, vinyl acetate / crotonic acid copolymers, vinylpyrrolidone / vinyl acrylate copolymers, vinyl acetate / butyl maleate / isobornyl acrylate copolymers, methyl vinyl ether / maleic anhydride copolymers and esters thereof, uncrosslinked polyacrylic acids and polyacrylic acids crosslinked with polyols, acrylamidopropyl-trimethylammonium chloride /acrylate copolymers, octyl acrylamide/methyl methacrylate-tert-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers, polyvinylpyrrolidone, vinylpyrrolidone/vinyl acetate copolymers, vinylpyrrolidone/dimethylaminoethyl methacrylate/vinyl caprolactam terpolymers and also optionally derivatised cellulose ethers and silicones. Furthermore the polymers as described in EP 1093796 (pages 3-8, paragraphs 17-68) may be used.

Biogenic active ingredients

Biogenic active ingredients are to be understood as meaning, for example, tocopherol, tocopherol acetate, tocopherol palmitate, ascorbic acid, deoxyribonucleic acid, retinol, bisabolol, allantoin, phytantriol, panthenol, AHA acids, amino acids, ceramides, pseudoceramides, essential oils, plant extracts and vitamin complexes.

Deodorising active ingredients

As deodorising active ingredients there come into consideration, for example, anti-perspirants, for example aluminium chlorohydrates (see J. Soc. Cosm. Chem. 24, 281 (1973)). Under the trade mark Locron® of Hoechst AG, Frankfurt (FRG), there is available

commercially, for example, an aluminium chlorohydrate corresponding to formula $\text{Al}_2(\text{OH})_5\text{Cl} \times 2.5 \text{ H}_2\text{O}$, the use of which is especially preferred (see J. Pharm. Pharmacol. 26, 531 (1975)). Besides the chlorohydrates, it is also possible to use aluminium hydroxyacetates and acidic aluminium/zirconium salts. Esterase inhibitors may be added as further deodorising active ingredients. Such inhibitors are preferably trialkyl citrates, such as trimethyl citrate, tripropyl citrate, triisopropyl citrate, tributyl citrate and especially triethyl citrate (Hydagen CAT, Henkel), which inhibit enzyme activity and hence reduce odour formation. Further substances that come into consideration as esterase inhibitors are sterol sulfates or phosphates, for example lanosterol, cholesterol, campesterol, stigmasterol and sitosterol sulfate or phosphate, dicarboxylic acids and esters thereof, for example glutaric acid, glutaric acid monoethyl ester, glutaric acid diethyl ester, adipic acid, adipic acid monoethyl ester, adipic acid diethyl ester, malonic acid and malonic acid diethyl ester and hydroxycarboxylic acids and esters thereof, for example citric acid, malic acid, tartaric acid or tartaric acid diethyl ester. Antibacterial active ingredients that influence the germ flora and kill or inhibit the growth of sweat-decomposing bacteria can likewise be present in the preparations (especially in stick preparations). Examples include chitosan, phenoxyethanol and chlorhexidine gluconate. 5-chloro-2-(2,4-dichlorophenoxy)-phenol (Triclosan, Irgasan, Ciba Specialty Chemicals Inc.) has also proved especially effective.

Anti-dandruff agents and film formers

As anti-dandruff agents there may be used, for example, climbazole, octopirox and zinc pyridithione. Customary film formers include, for example, chitosan, microcrystalline chitosan, quaternised chitosan, polyvinylpyrrolidone, vinylpyrrolidone/vinyl acetate copolymers, polymers of quaternary cellulose derivatives containing a high proportion of acrylic acid, collagen, hyaluronic acid and salts thereof and similar compounds.

Antioxidants

In addition to the primary light-protective substances it is also possible to use secondary light-protective substances of the antioxidant kind that interrupt the photochemical reaction chain triggered when UV radiation penetrates the skin or hair. Typical examples of such antioxidants are amino acids (e.g. glycine, histidine, tyrosine, tryptophan) and derivatives thereof, imidazoles (e.g. urocanic acid) and derivatives thereof, peptides, such as D,L-carnosine, D-carnosine, L-carnosine and derivatives thereof (e.g. anserine), carotinoids, carotenes, lyco-

pene and derivatives thereof, chlorogenic acid and derivatives thereof, lipoic acid and derivatives thereof (e.g. dihydrolipoic acid), aurothioglycose, propylthiouracil and other thiols (e.g. thioredoxin, glutathione, cysteine, cystine, cystamine and the glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl, lauryl, palmitoyl, oleyl, linoleyl, cholesteryl and glyceryl esters thereof) and also salts thereof, dilauryl thiodipropionate, distearyl thiodipropionate, thiodipropionic acid and derivatives thereof (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts) and also sulfoximine compounds (e.g. buthionine sulfoximines, homocysteine sulfoximine, buthionine sulfones, penta-, hexa-, hepta-thionine sulfoximine), also (metal) chelating agents (e.g. hydroxy fatty acids, palmitic acid, phytic acid, lactoferrin), hydroxy acids (e.g. citric acid, lactic acid, malic acid), humic acid, bile acid, bile extracts, bilirubin, biliverdin, EDTA, EDDS, EGTA and derivatives thereof, unsaturated fatty acids and derivatives thereof (e.g. linolenic acid, linoleic acid, oleic acid), folic acid and derivatives thereof, ubiquinone and ubiquinol and derivatives thereof, vitamin C and derivatives (e.g. ascorbyl palmitate, magnesium ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (e.g. vitamin E acetate), vitamin A and derivatives (e.g. vitamin A palmitate) and also coniferyl benzoate of benzoin resin, rutinic acid and derivatives thereof, glycosylrutin, ferulic acid, furfurylidene glucitol, carnosine, butyl hydroxytoluene, butyl hydroxyanisole, nordihydroguaiaretic acid, trihydroxybutyrophenone, uric acid and derivatives thereof, mannose and derivatives thereof, superoxide dismutase, N-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl]sulfanilic acid (and salts thereof, for example the disodium salts), zinc and derivatives thereof (e.g. ZnO, ZnSO₄), selenium and derivatives thereof (e.g. selenium methionine), stilbene and derivatives thereof (e.g. stilbene oxide, trans-stilbene oxide) and the derivatives suitable according to the invention (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids) of those mentioned active ingredients. HALS ("Hindered Amine Light Stabilizers") compounds may also be mentioned. The amount of antioxidants present is usually from 0.001 to 30 % by weight, preferably from 0.01 to 3 % by weight, based on the weight of the UV absorber of formula (1).

Hydrotropic agents

To improve the flow behaviour it is also possible to employ hydrotropic agents, for example ethoxylated or non ethoxylated mono-alcohols, diols or polyols with a low number of carbon atoms or their ethers (e.g. ethanol, isopropanol, 1,2-dipropenediol, propyleneglycol, glycerin, ethylene glycol, ethylene glycol monoethylether, ethylene glycol monobutylether, propylene

glycol monomethylether, propylene glycol monoethylether, propylene glycol monobutylether, diethylene glycol monomethylether; diethylene glycol monoethylether, diethylene glycol monobutylether and similar products). The polyols that come into consideration for that purpose have preferably from 2 to 15 carbon atoms and at least two hydroxy groups. The polyols may also contain further functional groups, especially amino groups, and/or may be modified with nitrogen. Typical examples are as follows: glycerol, alkylene glycols, for example ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol and also polyethylene glycols having an average molecular weight of from 100 to 1000 Dalton; technical oligoglycerol mixtures having an intrinsic degree of condensation of from 1.5 to 10, for example technical diglycerol mixtures having a diglycerol content of from 40 to 50 % by weight; methylol compounds, such as, especially, trimethylolethane, trimethylolpropane, trimethylolbutane, pentaerythritol and dipentaerythritol; lower alkyl-glucosides, especially those having from 1 to 8 carbon atoms in the alkyl radical, for example methyl and butyl glucoside; sugar alcohols having from 5 to 12 carbon atoms, for example sorbitol or mannitol; sugars having from 5 to 12 carbon atoms, for example glucose or saccharose; amino sugars, for example glucamine; dialcohol amines, such as diethanolamine or 2-amino-1,3-propanediol.

Preservatives and Bacteria-inhibiting agents

Suitable preservatives include, for example, methyl-, ethyl-, propyl-, butyl- parabens, benzalconium chloride, 2-bromo-2-nitro-propane-1,3-diol, dehydroacetic acid, diazolidinyl Urea, 2-dichloro-benzyl alcohol, DMDM hydantoin, formaldehyde solution, methyldibromoglutanitrile, phenoxyethanol, sodium hydroxymethylglycinate, imidazolidinyl urea, triclosan and further substance classes listed in the following reference: K.F.DePolo – A short textbook of cosmetology, Chapter 7, Table 7-2, 7-3, 7-4 and 7-5, p210-219.

Bacteria-inhibiting agents

Typical examples of bacteria-inhibiting agents are preservatives that have a specific action against gram-positive bacteria, such as 2,4,4'-trichloro-2'-hydroxydiphenyl ether, chlorhexidine (1,6-di(4-chlorophenyl-biguanido)hexane) or TCC (3,4,4'-trichlorocarbanilide). A large number of aromatic substances and ethereal oils also have antimicrobial properties. Typical examples are the active ingredients eugenol, menthol and thymol in clove oil, mint oil and thyme oil. A natural deodorising agent of interest is the terpene alcohol farnesol (3,7,11-tri-

methyl-2,6,10-dodecatrien-1-ol), which is present in lime blossom oil. Glycerol monolaurate has also proved to be a bacteriostatic agent. The amount of the additional bacteria-inhibiting agents present is usually from 0.1 to 2 % by weight, based on the solids content of the preparations.

Perfume oils

There may be mentioned as perfume oils mixtures of natural and/or synthetic aromatic substances. Natural aromatic substances are, for example, extracts from blossom (lilies, lavender, roses, jasmine, neroli, ylang-ylang), from stems and leaves (geranium, patchouli, petitgrain), from fruit (aniseed, coriander, caraway, juniper), from fruit peel (bergamot, lemons, oranges), from roots (mace, angelica, celery, cardamom, costus, iris, calmus), from wood (pine-wood, sandalwood, guaiacum wood, cedarwood, rosewood), from herbs and grasses (tarragon, lemon grass, sage, thyme), from needles and twigs (spruce, pine, Scots pine, mountain pine), from resins and balsams (galbanum, elemi, benzoin, myrrh, olibanum, opoponax). Animal raw materials also come into consideration, for example civet and castoreum. Typical synthetic aromatic substances are, for example, products of the ester, ether, aldehyde, ketone, alcohol or hydrocarbon type. Aromatic substance compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert-butylcyclohexyl acetate, linalyl acetate, dimethylbenzylcarbonyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethylmethylphenyl glycinate, allylcyclohexyl propionate, styryl propionate and benzyl salicylate. The ethers include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals having from 8 to 18 hydrocarbon atoms, citral, citronellal, citronellyl oxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilyal and bourgeonal; the ketones include, for example, the ionones, isomethylionone and methyl cedryl ketone; the alcohols include, for example, anethol, citronellol, eugenol, isoeugenol, geraniol, linalool, phenyl ethyl alcohol and terpinol; and the hydrocarbons include mainly the terpenes and balsams. It is preferable, however, to use mixtures of various aromatic substances that together produce an attractive scent. Ethereal oils of relatively low volatility, which are chiefly used as aroma components, are also suitable as perfume oils, e.g. sage oil, camomile oil, clove oil, melissa oil, oil of cinnamon leaves, lime blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil, labolanum oil and lavandin oil. Preference is given to the use of bergamot oil, dihydromyrcenol, lilyal, lylal, citronellol, phenyl ethyl alcohol, hexyl cinnamaldehyde, geraniol, benzyl acetone, cyclamen aldehyde, linalool, boisambrene forte, ambro-

xan, indole, hedione, sandelice, lemon oil, tangerine oil, orange oil, allyl amyl glycolate, cyclovertal, lavandin oil, muscatel sage oil, damascone, bourbon geranium oil, cyclohexyl salicylate, vertofix coeur, iso-E-Super, Fixolide NP, evernyl, iraldein gamma, phenylacetic acid, geranyl acetate, benzyl acetate, rose oxide, romillat, irotyl and floramat alone or in admixture with one another.

Colourants

There may be used as colourants the substances that are suitable and permitted for cosmetic purposes, as compiled, for example, in the publication "Kosmetische Färbemittel" of the Farbstoffkommission der Deutschen Forschungsgemeinschaft, Verlag Chemie, Weinheim, 1984, pages 81 to 106. The colourants are usually used in concentrations of from 0.001 to 0.1 % by weight, based on the total mixture.

Other adjuvants

It is furthermore possible for the cosmetic preparations to contain, as adjuvants, anti-foams, such as silicones, *structurants*, such as maleic acid, *solubilisers*, such as ethylene glycol, propylene glycol, glycerol or diethylene glycol, opacifiers, such as latex, styrene/PVP or styrene/acrylamide copolymers, complexing agents, such as EDTA, NTA, alaninediacetic acid or phosphonic acids, *propellants*, such as propane/butane mixtures, N₂O, dimethyl ether, CO₂, N₂ or air, so-called coupler and developer components as oxidation dye precursors, *reducing agents*, such as thioglycolic acid and derivatives thereof, thiolactic acid, cysteamine, thiomalic acid or mercaptoethanesulfonic acid, or oxidising agents, such as hydrogen peroxide, potassium bromate or sodium bromate.

Suitable insect repellents are, for example, N,N-diethyl-m-toluamide, 1,2-pentanediol or insect repellent 3535; suitable self-tanning agents are, for example, dihydroxyacetone and/or erythrulose or dihydroxy acetone and/or dihydroxy acetone precursors as described in WO 01/85124 and/or erythrulose.

Polymeric beads or hollow spheres as SPF enhancers

The combination of the UV-absorbers and UV-absorber combinations, listed above, with SPF enhancers, such as non-active ingredients like styrene/acrylates copolymer, silica beads, spheroidal magnesium silicate, crosslinked polymethylmethacrylates (PMMA ; Micopearl

M305 Seppic), can maximize better the UV protection of the sun products. Holosphere additives (Sunspheres® ISP, Silica Shells Kobo.) deflect radiation and the effective path length of the photon is therefore increased.(EP0893119). Some beads, as mentioned previously, provide a soft feel during spreading. Moreover, the optical activity of such beads, e.g. Micropearl M305, can modulate skin shine by eliminating reflection phenomena and indirectly may scatter the UV light. When formulated in O/W emulsions, the preferred amount of such SPF enhancers should represent 1% to 10% of the total amount of the emulsion.

Cosmetic or pharmaceutical preparations

Cosmetic or pharmaceutical formulations are contained in a wide variety of cosmetic preparations. There come into consideration, for example, especially the following preparations:

- skin-care preparations, e.g. skin-washing and cleansing preparations in the form of tablet-form or liquid soaps, soapless detergents or washing pastes,
- bath preparations, e.g. liquid (foam baths, milks, shower preparations) or solid bath preparations, e.g. bath cubes and bath salts;
- skin-care preparations, e.g. skin emulsions, multi-emulsions or skin oils;
- cosmetic personal care preparations, e.g. facial make-up in the form of day creams or powder creams, face powder (loose or pressed), rouge or cream make-up, eye-care preparations, e.g. eyeshadow preparations, mascara, eyeliner, eye creams or eye-fix creams; lip-care preparations, e.g. lipsticks, lip gloss, lip contour pencils, nail-care preparations, such as nail varnish, nail varnish removers, nail hardeners or cuticle removers;
- foot-care preparations, e.g. foot baths, foot powders, foot creams or foot balsams, special deodorants and antiperspirants or callus-removing preparations;
- light-protective preparations, such as sun milks, lotions, creams or oils, sunblocks or tropicals, pre-tanning preparations or after-sun preparations;
- skin-tanning preparations, e.g. self-tanning creams;
- depigmenting preparations, e.g. preparations for bleaching the skin or skin-lightening preparations;
- insect-repellents, e.g. insect-repellent oils, lotions, sprays or sticks;

- deodorants, such as deodorant sprays, pump-action sprays, deodorant gels, sticks or roll-ons;
- antiperspirants, e.g. antiperspirant sticks, creams or roll-ons;
- preparations for cleansing and caring for blemished skin, e.g. synthetic detergents (solid or liquid), peeling or scrub preparations or peeling masks;
- hair-removal preparations in chemical form (depilation), e.g. hair-removing powders, liquid hair-removing preparations, cream- or paste-form hair-removing preparations, hair-removing preparations in gel form or aerosol foams;
- shaving preparations, e.g. shaving soap, foaming shaving creams, non-foaming shaving creams, foams and gels, pre shave preparations for dry shaving, aftershaves or aftershave lotions;
- fragrance preparations, e.g. fragrances (eau de Cologne, eau de toilette, eau de parfum, parfum de toilette, perfume), perfume oils or perfume creams;
- cosmetic hair-treatment preparations, e.g. hair-washing preparations in the form of shampoos and conditioners, hair-care preparations, e.g. pretreatment preparations, hair tonics, styling creams, styling gels, pomades, hair rinses, treatment packs, intensive hair treatments, hair-structuring preparations, e.g. hair-waving preparations for permanent waves (hot wave, mild wave, cold wave), hair-straightening preparations, liquid hair-setting preparations, hair foams, hairsprays, bleaching preparations, e.g. hydrogen peroxide solutions, lightening shampoos, bleaching creams, bleaching powders, bleaching pastes or oils, temporary, semi-permanent or permanent hair colourants, preparations containing self-oxidising dyes, or natural hair colourants, such as henna or camomile.

Presentation forms

The final formulations listed may exist in a wide variety of presentation forms, for example:

- in the form of liquid preparations as a W/O, O/W, O/W/O, W/O/W or PIT emulsion and all kinds of microemulsions,
- in the form of a gel,
- in the form of an oil, a cream, milk or lotion,
- in the form of a powder, a lacquer, a tablet or make-up,
- in the form of a stick,

- in the form of a spray (spray with propellant gas or pump-action spray) or an aerosol,
- in the form of a foam, or
- in the form of a paste.

Of special importance as cosmetic preparations for the skin are light-protective preparations, such as sun milks, lotions, creams, oils, sunblocks or tropicals, pretanning preparations or after-sun preparations, also skin-tanning preparations, for example self-tanning creams. Of particular interest are sun protection creams, sun protection lotions, sun protection milk and sun protection preparations in the form of a spray.

Of special importance as cosmetic preparations for the hair are the above-mentioned preparations for hair treatment, especially hair-washing preparations in the form of shampoos, hair conditioners, hair-care preparations, e.g. pretreatment preparations, hair tonics, styling creams, styling gels, pomades, hair rinses, treatment packs, intensive hair treatments, hair-straightening preparations, liquid hair-setting preparations, hair foams and hairsprays. Of special interest are hair-washing preparations in the form of shampoos.

A shampoo has, for example, the following composition: from 0.01 to 5 % by weight of a UV absorber according to the invention, 12.0 % by weight of sodium laureth-2-sulfate, 4.0 % by weight of cocamidopropyl betaine, 3.0 % by weight of sodium chloride, and water ad 100%.

For example, especially the following hair-cosmetic formulations may be used:

- a₁) spontaneously emulsifying stock formulation, consisting of the UV absorber according to the invention, PEG-6-C₁₀oxoalcohol and sorbitan sesquioleate, to which water and any desired quaternary ammonium compound, for example 4 % minkamidopropyl dimethyl-2-hydroxyethylammonium chloride or Quaternium 80 is added;
- a₂) spontaneously emulsifying stock formulation consisting of the UV absorber according to the invention, tributyl citrate and PEG-20-sorbitan monooleate, to which water and any desired quaternary ammonium compound, for example 4 % minkamidopropyl dimethyl-2-hydroxyethylammonium chloride or Quaternium 80 is added;

- b) quat-doped solutions of the UV absorber according to the invention in butyl triglycol and tributyl citrate;
- c) mixtures or solutions of the UV absorber according to the invention with n-alkylpyrrolidone.

Other typical ingredients in such formulations are preservatives, bactericides and bacterio-static agents, perfumes, dyes, pigments, thickening agents, moisturizing agents, humectants, fats, oils, waxes or other typical ingredients of cosmetic and personal care formulations such as alcohols, poly-alcohols, polymers, electrolytes, organic solvents, silicon derivatives, emollients, emulsifiers or emulsifying surfactants, surfactants, dispersing agents, antioxidants, anti-irritants and anti-inflammatory agents etc.

Examples of cosmetic and pharmaceutical preparations (X = preferred combinations)

O/W systems:

Ingredients	1	2	3	4	5	6	7	8
Emulsifiers								
Potassium Cetyl Phosphate 2%-5%	X							
Cetearyl Alcohol/ Dicetyl Phosphate/Ceteth-10 Phosphate 2%-6%		X						
Sodium Stearyl Phthalamate 1%-2%			X					
Cetearyl Alcohol/Behentrimonium Methosulfate 1%-5%				X				
Quaternium-32 1%-5%					X			
Dimethicone copolyol/ Caprylic/Capric Triglyceride 1%-4%						X		
Steareth-2 /Steareth-21 2%-5%							X	
Polyglyceryl Methyl Glucose Distearate 1%-4%								X
Lipophilic emollient/dispersant oil 15%-20%	X	X	X	X	X	X	X	X
Fatty Alcohols and/or Waxes 1%-5%	X	X	X	X	X	X	X	X
Thickeners (water swellable thickeners) 0.5% - 1.5%	X	X	X	X	X	X	X	X
Preservatives 0.5% - 1%	X	X	X	X	X	X	X	X
Chelating agents (such as EDTA) 0%-0.2%	X	X	X	X	X	X	X	X
Antioxidants 0.05% - 0.2%	X	X	X	X	X	X	X	X
Water deionized Qs 100%	X	X	X	X	X	X	X	X
Perfume oils 0.1% - 0.4%	X	X	X	X	X	X	X	X
UV-absorber according to the invention 1% - 20%	X	X	X	X	X	X	X	X
UV-absorber as described in table 1-3 0% - 30%	X	X	X	X	X	X	X	X

W/O systems

<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
<u>Emulsifiers</u>					
Polyglyceryl-2 Dipolyhydroxystearate 2%-4%	X				
PEG-30 Dipolyhydroxystearate 2%-4%		X			
Rapeseed Oil Sorbitol Esters 1%-5%			X		
PEG-45/Dodecyl Glycol Copolymer 1%-5%				X	
Sorbitan Oleate / Polycerol-3 ricinoleate 1%-5%					X
Lipophilic emollient/dispersant oil 10% - 20%		X	X	X	X
Fatty Alcohols and/or Waxes 10% - 15%		X	X	X	X
Electrolytes (NaCl, MgSO ₄) 0.5% - 1%		X	X	X	X
Polyol phase (Propylene glycol, glycerin) 1% - 8%		X	X	X	X
Preservatives 0.3% - 0.8%		X	X	X	X
Perfume oils 0.1% - 0.4%		X	X	X	X
Chelating agents (such as EDTA) 0% - 0.2%		X	X	X	X
Antioxidants 0.05% - 0.2%		X	X	X	X
Water deionized Qs 100%		X	X	X	X
UV-absorber according to the invention 1% - 20%.		X	X	X	X
UV-absorber as described in table 1-3 0% - 30%.		X	X	X	X

W/Silicone systems

<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
<u>Emulsifiers</u>				
Dimethicone Copolyol / Cyclomethicone 5%-10%	X		X	
Laurylmethicone Copolyol 5%-10%		X		X
<u>Silicone phase</u>				
Cyclopentasiloxane 15%-25%	X			X
Dimethicone 15%-25%		X	X	
<u>Silicone elastomer</u>				
Dimethicone/Vinyldimethicone Crosspolymer 1%-10%	X	X	X	X
<u>Humectant/polyols</u> (Propylene glycol, glycerin) 2%-8%	X	X	X	X
<u>Chelating agents</u> (such as EDTA) 0%-0.2%	X	X	X	X
<u>Antioxidants</u> 0.05%-0.2%	X	X	X	X
<u>Preservatives</u> 0.3%-0.8%	X	X	X	X
<u>Perfume oils</u> 0.1%-0.4%	X	X	X	X
<u>Water deionized</u> Qs 100%	X	X	X	X
<u>UV-absorber according to the invention</u> 1% - 20%	X	X	X	X
<u>UV-absorber as described in table 1-3</u> 0%-30%	X	X	X	X

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Ingredients	1	2	3	4	5	6	7	8
Hydrocarbon oils					X		X	
Silicone oils						X		X
Preservatives 0.3% - 0.8%	X	X	X	X	X	X	X	X
Water deionized Qs 100%	X	X	X	X	X	X	X	X
Non ionic multifunctional W/O emulsifier 2%-5%	X	X	X	X	X	X	X	X
Waxes 1%-5%	X	X	X	X	X	X	X	X
Oil phase 20%-30%	X	X	X	X	X	X	X	X
Fatty acid esters								
Natural and synthetic Triglycerides								
Hydrocarbon oils								
Silicone oils								
Primary emulsion O1/W 15%	X	X	X	X	X	X	X	X
Electrolytes (NaCl, MgSO ₄) 0.1%-0.5%	X	X	X	X	X	X	X	X
Water deionized Qs 100%	X	X	X	X	X	X	X	X
Perfume oils 0.1%-0.4%	X	X	X	X	X	X	X	X
UV-absorber according to the invention 1%-20%	X	X	X	X	X	X	X	X
UV-absorber as described in table 1-3 0%-30%	X	X	X	X	X	X	X	X

Microemulsions

[illegible]

O/W Spray emulsions

G – Aqueous

[illegible]

[illegible]

Ingredients	1	2	3	4	5	6	7	8	9	10
UV-absorber as described in table 1-3 0%-30%	X	X	X	X	X	X	X	X	X	X

Light/dry cosmetic oils

Ingredients	1	2	3	4
<u>Lipophilic base</u>				
Hydrocarbon oils 30%-70%	X			X
Fatty acid esters branched or not 10%-50%		X	X	
<u>Light feel agent</u>				
Silicones/Siloxanes 0% - 10%	X		X	
Perfluorinated oils and Perfluoroethers 0%-10%		X		X
Viscosifying agents 0%-10%	X	X	X	X
<u>Waxes</u>				
Esters of long chain acids and alcohols 0% - 2%	X	X	X	X
Antioxidants 0.1%-1%	X	X	X	X
Solubilisants/dispersing agents 0%-5%	X	X	X	X
Perfume oils 0.1%-0.5%	X	X	X	X
UV-absorber according to the invention 1%-20%.	X	X	X	X
UV-absorber as described in table 1-3 0%-30%	X	X	X	X

Foaming/mousse products

Ingredients	
SD Alcohol 40 0%-8%	X
Propellant 8%-15%	X
Nonionic Emulsifier/Surfactant 0.5% - 3%	X
Corrosion Inhibitor 0% - 1%	X
Perfume oils 0.1% - 0.5%	X
Preservatives 0.1%-1%	X
Miscellaneous 0%-1%	X
UV-absorber according to the invention 1%-20%.	X
UV-absorber as described in table 1-3 0%-30%	X

Stick products

Ingredients	
Waxes 15%-30%	X
Natural and silicone oils 20%-75%	X
Lanoline derivatives 5%->50%	X

Ingredients	
Esters of lanolin	x
Acetylated lanolin	x
Lanolin oil	x
Colorants and pigments 10% - 15%	X
Antioxidants 0.1% - 0.8%	X
Perfume oils 0.1% - 2%	X
Preservatives 0.1%-0.7%	X
UV-absorber according to the invention 1%-20%	X
UV-absorber as described in table 1-3 0%-30%	X

Liquid and compact

Ingredients	1	2
<u>Liquid foundation</u>		
Powder phase 10%-15%	X	
Oil phase 30% - 40%; 75% (only for anhydrous form)	X	
Thickener/suspending agents 1%-5%	X	
Film forming polymers 1%-2%	X	
Antioxidants 0.1% - 1%	X	
Perfume oils 0.1% - 0.5%	X	
Preservatives 0.1%-0.8%	X	
Water deionized Qs 100%		
<u>Compact powder</u>		
Powder phase 15%-50%		X
Oil phase 15% - 50%		X
Polyol phase 5% - 15%		X
Antioxidants 0.1%-1%		X
Perfume oils 0.1% - 0.5%		X
Preservatives 0.1%-0.8%		X
<u>For the two product forms</u>		
UV-absorber according to the invention 1%-20%	X	X
UV-absorber as described in table 1-3 0%-30%	X	X

Conditioning Shampoos

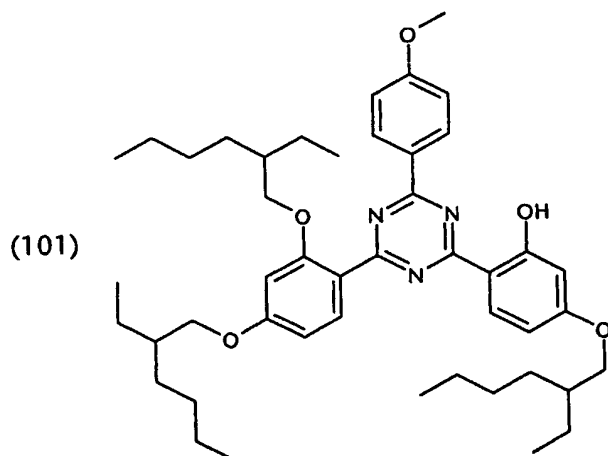
Ingredients	1
Primary surfactants (listed previously) 5%-10%	X
Secondary surfactants (listed previously) 5%-15%	X
Foam Stabilizers (listed previously) 0%-5%	X
Water deionized 40%-70%	X
Actives 0 -10%	x
Conditioners	x
Refatting agents	x
Moisturizing agents	x

Ingredients	1
Thickeners/Rheology modifiers 0%-3%	X
Humectants 0 %-2%	X
PH adjusting agents 0 %-1%	X
Preservatives 0.05 %-1%	X
Perfume oils 0.1%-1%	X
Antioxidants 0.05 %-0.20%	X
Chelating Agents (EDTA) 0%-0.2%	X
Opacifying agents 0%-2%	X
UV-absorber according to the invention 1%-20%	X
UV-absorber as described in table 1-3 0%-30%	X

The cosmetic preparation according to the invention is distinguished by excellent protection of human skin against the damaging effect of sunlight.

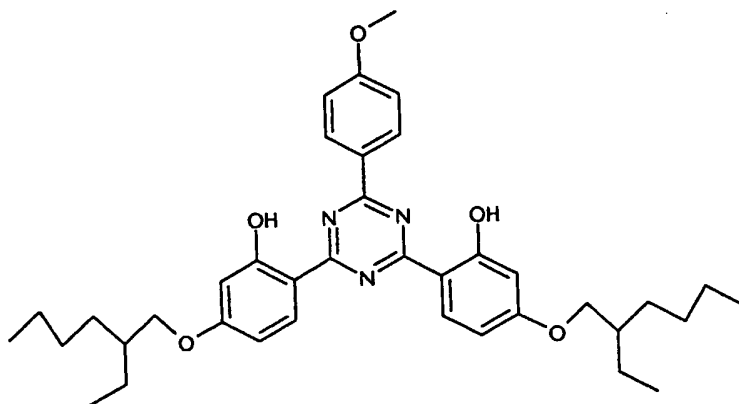
In the Examples that follow percentages refer to weight. In the case of the triazine derivatives the amounts used refer to the pure substance.

Example 1: Preparation of 2-((2,4-(2-ethyl-hexyloxy)-phenyl))-4-((2-hydroxy-4-(2-ethyl-hexyloxy)-phenyl))-6-(4-methoxyphenyl)-(1,3,5)-triazine



31.5 g of 2,4-bis((4-(2-ethyl-hexyloxy)-2-hydroxy)-phenyl))-6-(4-methoxyphenyl)-(1,3,5)-triazine of formula

(101a)



200 g of dimethylformamide and 13.5 g of sodium methanolate solution (30 %) are introduced into a reaction flask. The contents of the flask are slowly heated, with stirring, to the boiling temperature of dimethylformamide (155°C), with methanol being removed from the reaction mass by a separator. The contents of the flask are then cooled to 80°C and 14.7 g of 3-bromomethylheptane are added. The reaction mass is stirred at 80°C for 14 hours. For complete alkylation, 5 g of 3-bromomethylheptane are subsequently added and the reaction is continued at 80°C for 6 hours.

1500 ml of water and 8 g of formic acid are added to the reaction mass and the organic phase is taken up in about 300 ml of toluene. The toluene solution is concentrated by evaporation at 80°C *in vacuo* (0.5 mbar) (residue 37.4 g).

The pure compound (practically colourless crystals; m.p.= 53-55°C) can be obtained by crystallisation from 2-butanol.

This compound has outstanding solubility in

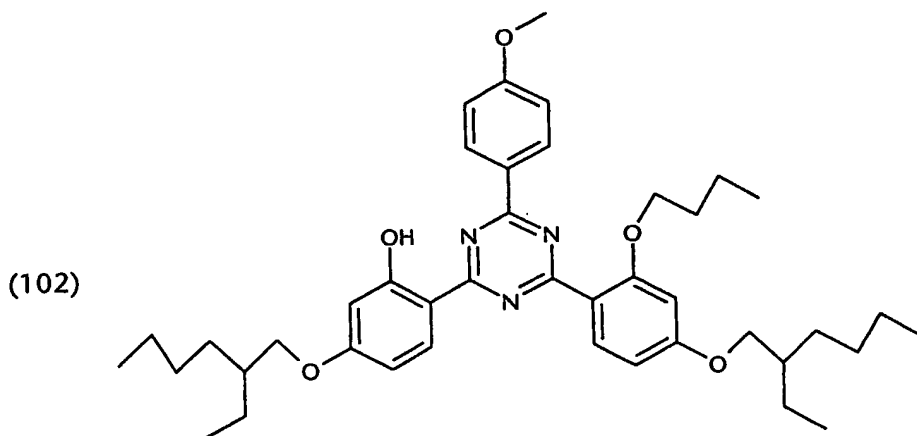
- glyceryl-trioctanoate > 30 % and
- di-C₁₂-C₁₃alkylmalates > 25 %.

Spectral properties:

λ_{max}	322 nm
ϵ	50443 litres/ (mol/cm)
E [1%, 1cm] (in dioxane)	681.62

Example 2:

Analogously to Example 1, compound (101a) is alkylated using butyl bromide (13.9 g). 34 g of the compound of formula



are obtained.

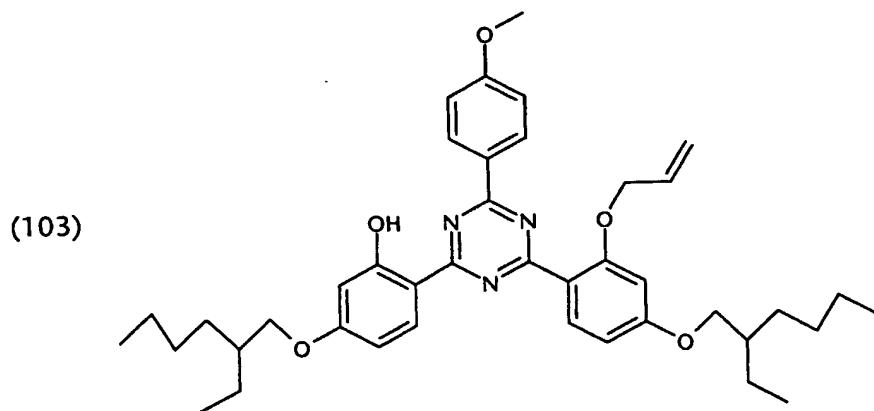
Analytical data:

Empirical: C = 74.1 % ; H = 8.7 % ; N = 5.9 %

(Theoretical: C = 73.8 % ; H = 8.4 % ; N = 6.1 %)

Example 3:

As described in Example 1, the compound of formula (101a) is alkylated using allyl bromide (12 g). 32 g of the compound of formula



are obtained.

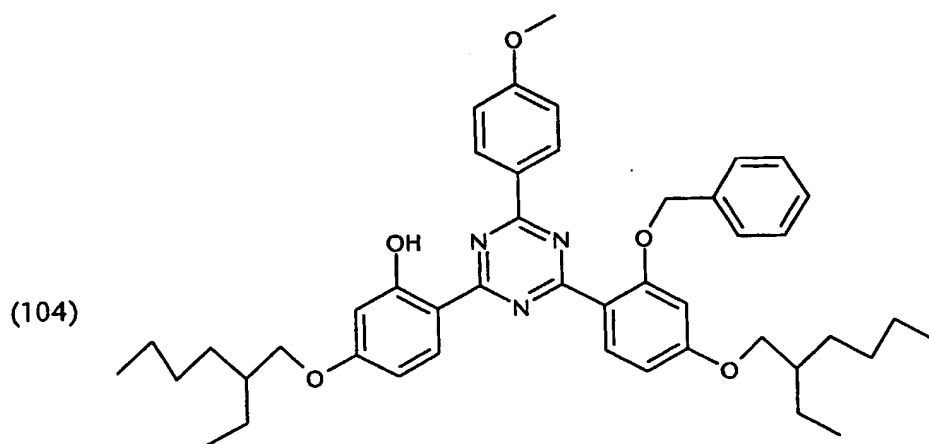
Analytical data:

Empirical: C = 73.8 % ; H = 8.2 % ; N = 5.9 %

(Theoretical: C = 73.7 % ; H = 8.0 % ; N = 6.3 %)

Example 4:

On alkylation of the compound of formula (101a) with benzyl bromide (10.3 g) according to Preparation Example 1, 35.7 g of the compound of formula



are obtained.

Analysis of the crude product shows:

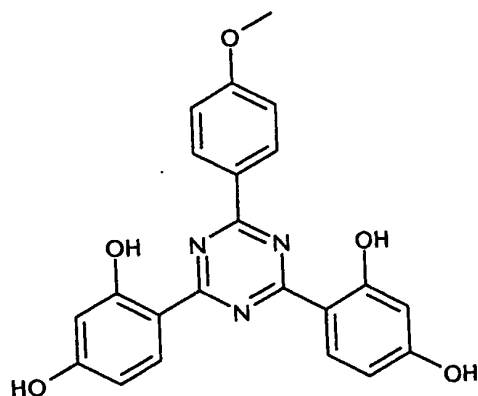
Empirical: C = 75.8 % ; H = 7.99 % ; N = 5.7 %

(Theoretical: C = 75.3 % ; H = 7.7 % ; N = 5.8 %)

Example 5:

20.2 g (0.05 mol) of 2,4-bis(2,4-dihydroxyphenyl)-6-(4-methoxyphenyl)-1,3,5-triazine of formula

(101b)



are introduced, together with 200 ml of Methylcellosolve (Merck®) and 8.8 g (0.11 mol) of 50 % sodium hydroxide solution, into a 500 ml sulfonation flask provided with a stirrer, dropping funnel, condenser and internal thermometer. Stirring is carried out at 80°C for 30 minutes and, at the same temperature, 23.2 g (0.12 mol) of 3-bromomethylheptane, dissolved in 25 ml of Methylcellosolve, are slowly added dropwise. The alkylation can be monitored by means of thin-layer chromatography. After reacting for 8 hours at 112-114°C, the starting material can no longer be detected. Concentration to dryness by evaporation is carried out, the residue is taken up in 100 ml of toluene/hexane (7 vol./3 vol.) and filtration is carried out to remove the insoluble material. For the purpose of purification, chromatography is carried out on silica gel (column: diameter = 5 cm, length = 60 cm). The compound of formula (101a) is obtained in the form of a viscous, light-yellow resin which crystallises out after a few weeks. Yield: 24.6 g (78.4 % of theory). Crystallisation can be accelerated by adding seed crystals.

In addition to the bisalkylated compound of formula (101a), about 1.4 g of the trisalkylated compound of formula (101) are formed in the reaction. The latter compound can be separated off as a by-product during column chromatography of the reaction mass.

Examples 6 to 8:

Analogously to Example 3, 90 parts of the compound of formula (101a) can be used in combination with

- 10 parts of the compound of formula (102) (= Example 6),
- 10 parts of the compound of formula (103) (= Example 7), or
- 10 parts of the compound of formula (104) (= Example 8).

Application Examples

Examples of use for cosmetic light protection

The light protection factors were determined by the method of Diffey and Robson, J. Soc. Cosmet. Chem. 40, 127 - 133 (1989) using an SPF analyser (Optometrix, SPF 290).

For the determination of photostability, the filter substances are dissolved in ethanol ($c = 1 \cdot 10^{-5} - 5 \cdot 10^{-5} \text{ M}$) and irradiated in a quartz cell, with stirring, using a metal halide lamp (Macam) ($I_{\text{UVB}} = 0.4 - 8.0 \text{ mW/cm}^2$). For conversion to the solar spectrum (CIE D65 standard daylight, standardised to $I_{\text{UVB}} = 0.127 \text{ mW/cm}^2$), the integral over the products of the wavelength-resolved lamp intensity and the corresponding absorption values of the UV absorber in question between 290 and 400 nm is calculated and divided by the integral over the products of the D65 light intensities and the corresponding absorption values of the UV absorber in question in the range between 290 and 400 nm. That factor is multiplied by the half-life value for degradation under irradiation with the metal halide lamp in order to obtain the corresponding half-life value under solar irradiation. The half-life value for photo-degradation under lamp irradiation is determined by UV spectroscopic measurement of the extinction at the wavelength of maximum absorbance and subsequent exponential fit. Using the method described, there are accordingly obtained the half-life values for photo-degradation in D65 light.

Example 9: O/W emulsion comprising the compounds of formulae (101), (103) and (106)

(A):

UV absorber mixture consisting of	
95 % by weight of the compound of formula (101a) and	3 g
5 % by weight of the compound of formula (101)	10 g
sesame oil	4 g
glyceryl stearate	1 g
stearic acid	0.5 g
cetyl alcohol	0.2 g
polysorbate 20	

(B):

propylene glycol	4 g
propylparaben	0.05 g
methylparaben	0.15 g
triethanolamine	0.1 g
carbomer 934	0.1 g
water	ad 100 ml

Preparation of the emulsionPhase (A):

Firstly, the UV absorber mixture is dissolved in sesame oil. The other components of (A) are added thereto and combined.

Phase (B):

Propylparaben and methylparaben are dissolved in propylene glycol. 60 ml of water are then added, heating to 70°C is carried out and then carbomer 934 is emulsified therein.

Emulsion:

(A) is slowly added to (B) with vigorous application of mechanical energy. The volume is adjusted to 100 ml by the addition of water.

The sun protection factors and photostability values determined are given in Table 2.

<u>Table 2:</u>	<u>Concen- tration</u>	<u>Sun protection factor*)</u>	<u>Photo- stability**) [h]</u>
UV absorber mixture consisting of 95 % by weight of the compound of formula (101a) and 5 % by weight of the compound of formula (101)	3 %	9.1	1500

*) according to Diffey and Robson

**) as half-life value of photo-degradation in D65 light in ethanolic solution

The sun protection factor can be varied by means of the UV absorber concentration.

The results show that the active substance mixture has a high photostability and that a good sun protection factor can be obtained when even a low concentration is used.

Example 10: Daily Care Cream, type O/W

	<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
Part A	Glyceryl Stearate (and) Cetearyl Alcohol (and) Cetyl Palmitate (and) Cocoglycerides	4.0
	Ceteareth-12	4.0
	Cetearyl Alcohol	2.0
	Dicaprylyl Ether	4.5
	Ethylhexyl Stearate	4.0
	Hexyl Laurate	3.5
	Ethylhexyl Triazone	1.0
	Benzylidene Malonate Polysiloxane	2.0
	HDI/Trimethylol Hexyl-Lactone Crosspolymer (and) Silica	5.0
	Stearyl Dimethicone	1.0
	Dimethicone	2.0
	Cetyl Alcohol	0.8
	Mixture of 80% of the compound of formula (101) and 20% of the compound of formula (101a)	2.0
		qs to 100
Part B	Water	
	Water (and) Scleroglucan (and) Phenoxyethanol	2.0
	Glycerin	2.0
Part C	Steareth-10 Allyl Ether/Acrylates Copolymer	0.45
	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.7
Part D	Aqua (and) Tocopheryl Acetate (and) Caprylic/Capric Triglyceride (and) Polysorbate 80 (and) Lecithin	4.0
Part E	Water (and) Sodium Hydroxide	qs
	Fragrance	qs

Manufacturing instruction:

Part A and part B are heated separately to 80°C. Part A is poured into part B under continuous stirring. Afterwards the mixture is homogenized with an Ultra Turrax at 11 000

rpm for 20 sec. The mixture is cooled down to 60°C and part C is added. Below 30°C part D is added and pH value is adjusted with sodium hydroxide between 6.5 and 7.0. Finally Fragrance is added.

Example 11: Sun Protection Cream, type O/W

<u>INCI-Name</u>		<u>% w/w (as supplied)</u>
Part A	Polyglyceryl-3 Methylglucose Distearate	2.0
	Decyl Oleate	5.7
	Isopropyl Palmitate	5.8
	Caprylic/Capric Triglyceride	6.5
	Mixture of 80% of the compound of formula (101) and 20% of the compound of formula (101a)	2.0
	Ethylhexyl Methoxycinnamate	5.0
	Cetyl Alcohol	0.7
		3.0
Part B	Glycerin	0.3
	Carbomer	
	Water	qs to 100
Part C	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.5
Part D	Methylene Bis-Benzotriazolyl Tetramethylbutylphenol (and) Aqua	8.0
	(and) Decyl Glucoside (and) Propylene Glycol (and) Xanthan Gum	20.0
	Water	
Part E	Water (and) Sodium Hydroxide	qs
	Fragrance	qs

Manufacturing instruction

Part A and part B are heated separately to 75°C. Part A is poured into part B whilst stirring. The mixture is homogenized with an Ultra Turrax by 11 000 rpm for 15 sec. The mixture is cooled down to 60°C and part C and part D are incorporated. The mixture is homogenized for a short time again (5 sec./11 000 rpm) and further cooled down with a moderate stirring. At room temperature pH is adjusted with sodium hydroxide solution between 5.5 and 6.0. Finally Fragrance is added.

Example 12: Daily Care UV Protection Lotion

	<u>INCI-Name</u>	<u>% w/w</u> <u>(as supplied)</u>
Part A	Oleth-3 Phosphate	0.6
	Steareth-21	2.5
	Steareth-2	1.0
	Cetyl Alcohol	0.8
	Stearyl Alcohol	1.5
	Tribehenin	0.8
	Isohexadecane	8.0
	Mixture of 90% of the compound of formula (101) and 10% of the compound of formula (101a)	5.0
Part B	Water	qs to 100
	Glycerin	2.0
	Methylene Bis-Benzotriazolyl Tetramethylbutylphenol (and) Aqua (and) Decyl Glucoside (and) Propylene Glycol (and) Xanthan Gum	3.0
	Disodium EDTA	0.1
Part C	Water	20.0
	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15
	Propylene Glycol	4.0
Part D	Sodium Acrylates Copolymer (and) Paraffinium Liquidum (and) PPG-1 Trideceth-6	1.5
	Cyclopentasiloxane	4.5
	PEG-12 Dimethicone	2.0
	Tocopheryl Acetate	0.45
	Water (and) Citric Acid	Qs
Part E	Fragrance	Qs

Manufacturing instruction

Heat part A and part B separately up to 75°C. Pour part A into part B under continuous stirring. Immediately after the emulsification, incorporate in the mixture SF 1202 and SF 1288 from part D. Afterwards homogenize with an Ultra Turrax at 11000 rpm for 30 sec. Let cool down to 65°C and incorporate SALCARE® SC91. Under 50°C, add part C. At 35°C or below incorporate Vitamin E Acetate and subsequently adjust the pH with Citric Acid. At room temperature add part E.

Example 13: Sun Protection Cream, type O/W

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Polyglyceryl-3 Methylglucose Distearate	2.0
	Decyl Oleate	5.7
	Isopropyl Palmitate	5.8
	Caprylic/Capric Triglyceride	6.5
	Mixture of compound of formula (101) (90%) and Butyl-methoxydibenzoyl-methane (CAS# 70356-09-1) (10%)	2.0
	Ethylhexyl Methoxycinnamate	5.0
	Cetyl Alcohol	0.7
Part B	Glycerin	3.0
	Carbomer	0.3
	Water	qs to 100
Part C	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and)	0.5
	Butylparaben (and) Propylparaben (and) Isobutylparaben	
Part D	Methylene Bis-Benzotriazolyl Tetramethylbutylphenol (and) Aqua	8.0
	(and) Decyl Glucoside (and) Propylene Glycol (and) Xanthan Gum	
	Water	20.0
Part E	Water (and) Sodium Hydroxide	Qs
	Fragrance	Qs

Manufacturing instruction:

Part A and part B are heated separately to 75°C. Part A is poured into part B whilst stirring. The mixture is homogenized with an Ultra Turrax at 11 000 rpm for 15 sec. The mixture is cooled down to 60°C and part C and part D are incorporated. The mixture is homogenized for a short time again (5 sec./11 000 rpm). After cooling further down with a moderate stirring the pH is adjusted with sodium hydroxide at room temperature. A solution between pH 5.50 and 6.00 is obtained. Finally Fragrance is added.

Example 14: Sun Protection Cream, type O/W

<u>INCI-Name</u>		<u>% w/w</u> <u>(as supplied)</u>
Part A	Polyglyceryl-3 Methylglucose Distearate	2.0
	Decyl Oleate	5.7
	Isopropyl Palmitate	5.8
	Caprylic/Capric Triglyceride	6.5
	Mixture of the compound of formula (101) (90%) and Uvinul A Plus CAS# 302776-68-7 (10%)	2.0
	Ethylhexyl Methoxycinnamate	5.0
	Cetyl Alcohol	0.7
Part B	Glycerin	3.0
	Carbomer	0.3
	Water	qs to 100
Part C	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.5
Part D	Methylene Bis-Benzotriazolyl Tetramethylbutylphenol (and) Aqua	8.0
	(and) Decyl Glucoside (and) Propylene Glycol (and) Xanthan Gum	
	Water	20.0
Part E	Water (and) Sodium Hydroxide	Qs
	Fragrance	Qs

Manufacturing instruction:

Part A and part B are heated separately to 75°C. Part A is poured into part B whilst stirring. The mixture is homogenized with an Ultra Turrax at 11 000 rpm for 15 sec. After cooling down to 60°C part C and part D are incorporated. The mixture is homogenized for a short time again (5 sec./11 000 rpm). After cooling further down with a moderate stirring pH is adjusted at room temperature with sodium ydroxide solution between 5.50 and 6.00. Finally fragrance is added.

Example 15: Sun Protection Cream, type O/W

<u>INCI-Name</u>		<u>% w/w</u> <u>(as supplied)</u>
Part A	Polyglyceryl-3 Methylglucose Distearate	2.0
	Decyl Oleate	5.7
	Isopropyl Palmitate	5.8
	Caprylic/Capric Triglyceride	6.5
	Mixture of compound of formula (101) (90%) and Benzyliden Camphor, CAS# 36861-47-9 (10%)	2.0
	Ethylhexyl Methoxycinnamate	5.0
	Cetyl alcohol	0.7
		3.0
		0.3
Part B	Glycerin	
	Carbomer	
	Water	qs to 100
Part C	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.5
Part D	Methylene Bis-Benzotriazolyl Tetramethylbutylphenol (and) Aqua (and) Decyl Glucoside (and) Propylene Glycol (and) Xanthan Gum	8.0
	Water	20.0
Part E	Water (and) Sodium Hydroxide	Qs
	Fragrance	Qs

Manufacturing instruction

Part A and part B are heated separately to 75°C. Part A is poured into part B whilst stirring. The mixture is homogenized with an Ultra Turrax at 11 000 rpm for 15 sec. After cooling down to 60°C part C and part D are incorporated. The mixture is homogenized for a short time again (5 sec./11 000 rpm). After cooling further down with a moderate stirring pH is adjusted at room temperature with sodium hydroxide A solution between pH 5.50 and 6.00 is obtained. Finally Fragrance is added.